INTERNATIONAL LEAD ZINC RESEARCH ORGANIZATION, INC.



GALFAN TECHNICAL RESOURCE CENTER

2525 MERIDIAN PARKWAY POST OFFICE BOX 12036 RESEARCH TRIANGLE PARK, N.C. 27709-2036 TELEPHONE 361-4647 (AREA CODE 919) TELEX: 261533 FACSIMILE: (919) 361-1957

MEMORANDUM

- TO: Galfan® Licensees Galfan Licensee Meeting Attendees
- FROM: John L. Hostetler, P.E., Director Galfan Technical Resource Center
- DATE: 1 February 1993
- SUBJECT: •Minutes of 17th Licensee Meting Proceedings •Preliminary Plans for 18th Licensee Meeting

I apologize for the delay in getting these important minutes to you. The harder we tried to speed up the process, the more delays we seemed to create.

We have improved the reproduction quality of the publication and simplified the format. Your comments are invited for consideration as we begin planning the 18th meeting which will be held in Linz, Austria on October 4 and 5, 1993.

Many attendees have asked to have copies of the technical papers at the meeting. This is an objective for the 18th meeting. The formal Call for Papers will be sent out soon, but if you know you have a paper to present, please start with plans to submit it as soon as possible and to include original photography, art work, etc.



GALFAN™

IMPROVED GALVANIZING

17th LICENSEE MEETING PROCEEDINGS

October 12-14, 1992

Keidanren Kaikan International Conference Hall Tokyo, Japan

Sponsored by:

International Lead Zinc Research Organization, Inc. GALFAN Technical Resource Center Research Triangle Park, NC USA Proceedings of the

17th Meeting

of the

GALFAN LICENSEES

October 12-14, 1992

Keidanren Kaikan International Conference Hall Tokyo, Japan

Sponsored by

ILZRO/Galfan Technical Resource Center John Hostetler, Chairman

Local Committee:

Masao Hirano, Mitsubishi Materials Corp. Namio Hanawa, Kawasaki Steel Corp. Norihiko Usui, Kawatetsu Galvanizing Co., Ltd.

Tour Host:

Kawatetsu Galvanizing Co., Ltd.

Since last we met

This past year will be remembered in world history for the many unexpected events in the arenas of politics, economics, and knowledge. It was that sort of year for Galfan too. Part of this is undoubtedly caused by Galfan's rapid market growth and part is the ever accelerating speed at which information is discovered, developed, and put into use. For the record then, I offer seven statements which I think summarize the plan of action for Galfan's future.

We must translate our scientific knowledge of Galfan into technological expertise. Galfan researchers have discovered and recorded a priceless data base of knowledge which must now be converted into technologies of processes, process control, equipment design and information that can be mastered by engineers, technicians and operators. We must be even beyond this to show sales and marketing people how this scientific knowledge can benefit their customers. One of GTRC's efforts in this area is the new GALFAN MANUAL which will be introduced during this Meeting.

We must form partnerships with qualified Suppliers. Business relationships have already gone through radical changes and are due for more. This is easily seen in the automotive industry where the buyer-seller relationship has evolved from an adversarial one to a partnership concept. The results speak for themselves. GTRC is working to recognize and identify suppliers who have shown competence and attitudes that encourage and contribute to such relationships.

We must develop new process technologies. What is today's barrier to improve a product or to be able to make a product, become tomorrow's new product when the right process is discovered, developed or applied. I think this next year will see several completely new process technologies which will help Galfan by improving its product quality or expand the forms of products which can be coated with Galfan. GTRC is cooperating with suppliers and licensees who are experimenting and testing new ideas with great potential for Galfan.

We must open new market regions. To be truly successful, Galfan must be a truly worldwide product. Galfan Licensees in Japan, western Europe, and the United States are to be congratulated for having produced almost 1.5 million tons of Galfan coated steel in eight years, the same growth rate as for Galvalume's first eight years (but with a greater cooperative worldwide approach). GTRC has already initiated strategies to open eastern Europe, southeast Asia and China as new markets for Galfan. We must advance and expand our proven technology. It is a truism that the world will not beat a path to your door even if you have the best of anything unless you tell them about it. Galfan's first successes came from coating strip on continuous Sendzimer type galvanizing lines. Then came double-dipping for continuous flux type wire lines and still later, single dip electroflux for tubing. These processes are associated with particular forms but we know now that electroflux works on strip and it will surely work on wire with what we now know about the degree of cleanliness needed. GTRC is prepared to be creative in licensing new process/form applications in the interest of making Galfan more versatile.

We must promote the formation and active operation of Regional Galfan Development Associations. North America already has an association (NAGDA) in place and plans are well underway for EDGA in Europe but every region has unique marketing and technical situations known best by the licensees in the region. Some of the necessary technical and marketing tasks are more effective when done by an association rather than a single commercial producer. The Association offers an ideal interface between the region's licensees, between ILZRO and the licensees, and between the licensees and suppliers. Ideally, the Association will be totally licensee-driven with GTRC providing technical support and liasing with ILZRO.

Last but by no means least, we must continue to improve what we are already doing well. Almost half of Galfan appears in the marketplace as prepainted sheet. Galfan shows clear superiority in this application, especially if it is to be profiled. The growth of profiled prepainted (PPP) is touted to be the fastest growing single steel application for the near future. Galfan can be No. 1 but there will be fierce competition from Galvalume and others. GTRC plans to make prepaint the theme of next year's Licensee Meeting in Linz, Austria, so that we can all concentrate our attention on this application. This is not to say that unpainted Galfan is not a growth product. Quite to the contrary. We see huge market penetrations in the corrugated building panels, highway guardrails, fence systems, pipe and conduit, HVAC applications and nonspecification applications for galvanized sheet.

So we approach the next year with excitement and enthusiasm for the prospects of promoting and expanding the use of better and better Galfan to protect steel in many different forms.

Sincerely,

John L. Hostetler, Director Galfan Technical Resource Center

TABLE OF CONTENTS

Galfan® Action Plan List of Attendees Confidentiality Statement Welcome

PAPERS, REPORTS AND DISCUSSIONS

SECTION TITLE		PRESENTED BY:	
I	Report on Lehigh University's preliminary investigation of Fundamental Study on Grain Boundary Dents in Galfan	A. Stoneman ILZRO	
п	ILZRO Project ZM-285, Progress Report No. 26, Industrial Galfan Product Characterization Programme	V. LeRoy C.R.M.	
Ш	Corrosion Resistance of Unpainted Galfan Steel	J.L. Hostetler GTRC	
IV	Corrosion Resistance of Zn-5% Al Hot-Dip Coated Steel Sheets - 7-Year Outdoor Exposure Test Results	Y. Hirose Nisshin Steel (Repeat from 1990)	
v	Corrosion Resistance of Painted Zn-5% Al Coated Steel Sheet Exposed Outdoors for Nine Years	Y. Kobayashi Kawatetsu Galvanizing	
VI	A Corrosion Resistance Study of Post-Welded BEZINAL (Galfan) Coated Wires	M. Dewitte N.V. Bekaert	
VII	New Developments in Galfan Coating on Wire and Small Parts	R. Nunninghoff Wuppertal Universitat	
VIII	Galfan/Al-Rich Paint Coating System for Welded Steel Automotive Tubing	J.D. Hostetler Decktec	
IX	Influence of Resistance Welding Tip Geometry on Tip Performance in Welding Zinc Coated Steel	R. Solomon SCM Metal Products	

SECTION	TITLE	PRESENTED BY:	
x	A New Acid-Type Surface Conditioning Treat- ment for Paint of Zn-4% Al-0.1% Mg Alloy Coated Steel Sheets	H. Mashihara Nisshin Steel	
XI	Progress Report from British Steel Welsh Labs Chrome-free Systems for Galfan	A. Stoneman ILZRO	
XII	Darkening of Galfan and Packing	I. Nagano Yodogawa Steel	
ХШ	Residual Mischmetal Dross Problem in a Dual- Purpose Galvanizing Line	N. Ueda Sumitomo Metal Ind.	
XIV	Report From: Galfan Bath Management Task Force	M. Dubois Cockerill Sambre	
XV	Surface Preparation Technology for Galfan	Y. Gerenrot Ferro Technologies	
XVI	Galfan Production on a Cook-Norteman (Flux) Hot Dipped Galvanizing Line	J. Rendos Wheeling-Pittsburgh	
XVII	Analysis of Galfan Coatings	R. Pankert Union Miniere	
XVIII	Hot Dipped Galvanized Steel Sheet with Zn/Al and Al/Zn Alloy Coating for Building and Appliance Industry	W. Schwarz Hoesch Stahl	
XIX	NAGDA Report	A. Celestin	
XX	EGDA Report	L. Pelini	

EXPLANATION

This year's Proceedings are published in a different format and style. We have not attempted to publish all of the commentary between papers although the entire proceedings are recorded on tape. If a Licensee has a serious need to know, a duplicate tape of a specified portion is available for a nominal reproduction cost.

The papers are printed as submitted by the authors. A record of the questions, answers, and discussion of the paper as presented to the meeting immediately follows the paper. Sections XII, XIV, and XVII were part of the Active Operator's Session. No minutes of this Session are published.

17th Galfan Licensees Meeting October 12-14, 1992 Tokyo, Japan

MEETING ATTENDEES

Name	Company	License

Aoyama, Kazuo	Kawasaki Steel Techno Wire	Wire
Arimura, Mitsushi	Kobe Steel Co., Ltd.	Sheet
Blankenship, Milton	Kohler Coating Machinery Corporation	Supplier
Capul, Anthony	Weirton Steel Corporation	Sheet
Celestin, Andy	Weirton Steel Corporation	Sheet
Decker, Charles	Decktec, Inc.	Supplier
DeWitte, Marc	N.V. Bekaert S.A.	Wire
DuBois, Michel	Cockerill Sambre	Sheet
Feron, Stephane	Cockerill Sambre, R&D	Sheet
Fukumoto, H.	Nisshin Steel Co., Ltd.	Sheet
Gerenrot, Yum	Ferro Technologies, Inc.	Supplier
Grimm, Russell	Wean Industries	Supplier
Hatano, Yasuhiro	Nippon Denro Mfg. Co., Ltd.	Supplier
Hiraishi, T.	Kawatetsu Galvanizing Co., Ltd.	Sheet
Hirano, Masao	Mitsubishi Materials Corp.	Alloy
Hoboh, Yoshihiko	Sumitomo Metal Ind., Ltd.	Sheet
Hostetler, John D.	Decktec, Inc.	Supplier
Hostetler, John L.	Int'l. Lead Zinc Research Org., Inc.	-
Inoue, Norio	NKK Corporation	Sheet
Irie, Toshio	Kawatetsu Galvanizing Co., Ltd.	Sheet
Johnson, Gordon L.	SCM Metal Products, Inc.	Supplier
Kakimoto, Akihiro	Mitsubishi Materials Co.	Alloy
Kato, C.	Kawasaki Steel Corporation	Sheet
Kawaguchi, Hiromitsu	Nisshin Steel Co., Ltd.	Sheet

Name	Company	License
Kobayashi, Eiji	Kawatetsu Galvanizing Co., Ltd.	Sheet
Kobayashi, Katuhiro	Nippon Denro Co., Ltd.	Supplier
Kobayashi, Shigeru	Kawasaki Steel Corporation	Sheet
Kobayashi, Yasuji	Kawatetsu Galvanizing Co., Ltd.	Sheet
Koga, Shinichi	Nisshin Steel Co., Ltd.	Sheet
Leroy, Vincent	Centre de Recherches Metallurgiques	Res. Contr
Maeda, Yoshihiko	Dowa Mining Co., Ltd.	Alloy
Malmgreen, John	Eastern Alloys	Alloy
Mateumoto, Shizuo	Kawasaki Steel Techno Wire	Wire
Messerly, R.H.	Wean Industries	Supplier
Nagano, I.	Yodogawa Steel Works	Sheet
Nagasaki, Hidenori	Mitsui Mining & Smelting Co.	Alloy
Nariyoshi, Yukio	Nisshin Steel Co., Ltd.	Sheet
Nunninghoff, Rolf	Univ. Wuppertal/Trefil ARBED	Wire
Ogura, Akihiro	Yodogawa Steel Works	Sheet
Okamoto, Kohei	Kobe Steel Co., Ltd.	Sheet
Oner, Marc	Union Miniere	Alloy
Pankert, Roger	Union Miniere	Alloy
Parrish, David	Wheeling-Pittsburgh Steel Corporation	Sheet
Pelini, Luciano	Cockerill Sambre S.A.	Sheet
Ranck, Tom	Ferro Technologies, Inc.	Supplier
Rendos, John	Wheeling-Pittsburgh Steel Corporation	Sheet
Shoji, Masahiro	NKK Corporation	Sheet
Solomon, Ronald R.	SCM Metal Products, Inc.	Supplier
Stoneman, Alan M.	Int'l. Lead Zinc Research Org., Inc.	-
Sugimoto, K.	Maruichi Steel Tube Ltd.	Tube
Sugimoto, Seii	Mitsui Mining & Smelting	Alloy
Tajuri, Yasuhisa	NKK Corporation	Sheet
Takasago, Y.	Maruichi Steel Tube Ltd.	Tube
Ueda, Naotaka	Sumitomo Metal Ind., Ltd.	Sheet
Williams, F. Graham	British Steel Plc U.K.	Sheet
Yoshimura, Yoshinori	Maruichi Steel Tube Ltd.	Tube

17th Galfan® Licensee Meeting October 12-14, 1992 — Tokyo

STATEMENT REGARDING CONFIDENTIALITY

Most of what is reported in these sessions will become public information but some must be considered *CONFIDENTIAL* and proprietary to ILZRO, a Galfan Licensee, or a Supplier.

Every company here has agreed to terms in a *Confidentiality Agreement* with ILZRO and as such, is legally and ethically bound to receive any information from these sessions under the terms of that Agreement.

One of the reasons for this policy is to encourage a safe exchange of information whether it comes from formal papers and reports or casual question and answer discussions.

The Proceedings of these sessions shall therefore be considered as confidential material.

We live in an information society. This group certainly knows the value of good information. The Licensee Meeting is a tremendously effective forum for transferring information but we need to be sure the information, usually hard won, profits the licensed group first.

WELCOME TO THE GALFAN® LICENSEES

by

Naohiko Soeda, General Manager Sheet & Strip Technology Kawasaki Steel Corporation

Good Morning Gentlemen.

Thank you Chairman Hostetler. I speak on behalf of the host company for this 17th Galfan® Licensee Meeting and the three Japanese companies who have prepared for this conference: Mitsubishi Materials Corporation, Kawasaki Steel, and Kawatetsu Galvanizing Corporation.

On the behalf of those companies, I would like to sincerely welcome all of you to the conference and to Japan. About one-third of you come from foreign countries. I estimate about 60 people are going to join this conference, more than 20 people from the North American and European countries. There are 25 Galfan licensees here, 13 from foreign countries and 12 from Japan.

This conference has been arranged by three companies but mainly Mr. Hirano of Mitsubishi Materials Corporation. May I introduce him. He has worked hard to prepare for this meeting. He will help you more if you need.

There are 15 technical papers which have been prepared for presentation and Kawatetsu Galvanizing has prepared a plant tour of their Chiba Works which is about one and a half hours travel from here. You will tour the plant on Wednesday, October 14th.

This is the third Galfan meeting in Japan. Six years ago, we had the 8th technical meeting here in Tokyo and three years ago the 13th meeting was held in Osaka. The middle of October is usually a good season of climate with clear skies in Japan but unfortunately this year it is not so pretty outside. It is cloudy like the economic situation in Japan.

On this day the economical conditions especially in the steel industry are not so clear and many people are very much interested in the new quota. In that point I am very much interested in this meeting. You will expand your process technology of Galfan and also you might find other markets and other business for Galfan here. I hope you will have deep discussions during your sessions and an interesting tour. I turn this meeting over to Mr. Hostetler, the Director of the Galfan Technical Resource Center.

Thank you very much.

17TH GALFAN LICENSEES MEETING

October 12-14, 1992 Tokyo, Japan

A Fundamental Investigation of The Occurrence of Grain Boundary Dents in Galfan

By: Professor A. Marder, Lehigh University

Presented By: Dr. Alan M. Stoneman (ILZRO)

Introduction

The object of this work is to investigate the nature of formation of grain boundary dents in Galfan and to determine how dents may be avoided. Gratitude is owed to NKK Corporation, Cockerill-Sambre, and Kawatetsu Galvanizing Company who have funded this work during 1992. By way of introduction to the subject, it may be stated that the results obtained to date have shown quite clearly that grain boundary dents are principally a feature of Galfan alloy solidification characteristics and appear to be associated with shrinkage, impurity segregation and cracking at eutectic nodule boundaries and triple points.

The approach at Lehigh has been to carry out solidification experiments to gain a more detailed characterization of the Galfan microstructure and to identify the role of factors such as eutectic cell and nodule size, lamellar spacing and structure, the relative volumes of the primary and secondary phases, and impurity segregation in relation to dent formation. Thus, it is intended to determine which factors have the greatest influence on denting and how this unwanted feature of Galfan production may be eliminated or at least controlled to an acceptable level. It is hoped that the results of this investigation will provide the basis for future hot dipping experiments in the laboratory under conditions which simulate the production of Galfan.

Background

It is well known that Galfan coatings may contain dents but it is perhaps somewhat surprising to find that these dents can be as much as 20 microns deep. The occurrence of such dents may render the coating unsuitable for a number of applications where surface appearance is of the utmost importance e.g., in the automotive industry. Previously, this problem has been attributed to the morphology of the eutectic lamellar with dents occurring at the junction of eutectic cells with different orientations. Denting has been observed in a range of Galfan alloys with aluminium compositions between 4 and 7% but the effect appears to be most severe at the eutectic composition of 5.2% aluminium. Thus, attempts to reduce the denting problem have tended to concentrate on reducing the aluminium content of the Galfan or increasing the solidification rate. As a result of these attempts, some improvement was reported but reducing aluminium content also tended to reduce corrosion resistance and ductility. Increasing the cooling rate reduced the size of the dents but tended to increase their number.

The approach at Lehigh has identified the solidification characteristics of the Galfan alloy as the key issue in dent formation and it is in this area that they have concentrated their not inconsiderable research capability.

Review of Work

A) Examination of As-Received Galfan

Initially an extensive examination of as-received commercial quality Galfan was carried out using scanning electron microscopy sometimes in polarized light. Figure 1 shows the Galfan coating on a commercially-produced sample with grain boundary dents evident at the eutectic nodule boundaries and triple points.

Figure 2 shows a crack at the eutectic nodule boundary with which Lehigh has been able to identify a number of white spots. These spots represent evidence of impurity segregation at the cracks and the dents and are in fact lead particles. This is confirmed by the results of analytical work shown later.

Figure 3 shows a schematic illustration of how Galfan solidification and growth may be interpreted. Growth commences with a zinc nucleus in the melt from which eutectic cells grow radially until they impinge on each other with the formation of a eutectic nodule or grain.

B) Polyethylene Oxide Solidification Experiments

The second aspect of the Lehigh work involved using polyethylene oxide in an attempt to model the solidification process for Galfan. The polyethylene oxide was melted on the glass slide, covered, and then allowed to solidify. A remarkable video is available showing clearly a solidification pattern which is very similar to that described in the previous slide and also demonstrates how voids can occur when the expanding spherulites of the polyethylene oxide impinge.

As the density of the solid is greater than that of the liquid, then the volume at the melt between the expanding particles is depleted. This may be expected to happen in any situation where the solid has a greater density and as the volume changes associated with solidification of zinc and aluminium are not insignificant, i.e., 4.7% and 6.5% respectively, it is perhaps not surprising that

shrinkage and cracking is observed in zinc-aluminium castings and also in Galfan. Consequently, cracking in Galfan may be expected to occur at the primary dendrite/eutetic boundary as shown in Figure 4 where a crack is observed running from the Galfan/steel interface to the surface of the Galfan between the eutectic primary zinc rich dendrites.

C) **Directional Solidification**

The third aspect of the Lehigh work involves a series of experiments which were carried out to determine the effects of directional solidification and alloy growth rate on the microstructural characteristics of the alloy. In these experiments, Galfan alloy at 4.9% aluminium was cast into 4 mm diameter rods and solidified in a vertical direction. Figure 5 shows the Galfan microstructure with the typical eutectic cell formation that may be associated with directional solidification. In connection with Figure 5 the schematic representation of alloy growth shown in Figure 3 should be borne in mind. The inter-lamellar spacings were found to be between 2.1 and 1.2 microns, for growth rates of between 18.6 and 112 microns per second which are shown to agree quite well with the data that has been produced by previous investigators. Figure 6 shows interlamellar spacing plotted against growth rate in microns per second with the Lehigh results given at the slow cooling rates. In Figure 7 the distance between the cells is plotted against growth rate. As expected the intercellular spacing decreases as the growth rate increases.

Figure 8 shows a Galfan microstructure in which aluminium rich dendrites are surrounded by halos of zinc. It is believed that segregation within the Galfan ingot accounts for the presence of aluminium rich dendrites in an alloy containing 4.9% aluminium which is on the zinc-rich side of the eutectic composition. As zinc has been nucleated by aluminium then this would suggest that aluminium is a more effective nucleant of zinc than zinc is of aluminium. In order to take this into account then the zinc-aluminium equilibrium diagram may be drawn with a zone of eutectic coupled growth displaced to the aluminium side as shown in Figure 9. The zone of eutectic coupled growth may be defined as an area where a wholly eutectic matrix is produced. Therefore, in order to obtain a completely eutectic structure at room temperature, it may be necessary to select an alloy which is richer in aluminium than the eutectic composition. The precise position of the zone of eutectic coupled growth may be very important with respect to our understanding of the solidification characteristics of the Galfan alloy and could provide more information about the role of primary dendrites with regard to microsegregation and shrinkage in Galfan.

D) Insitu Solidification Studies

The fourth aspect of the Lehigh work deals with insitu solidification studies. In this case Galfan samples were taken from an as-received ingot and melted at 400°C and then solidified at the rate of about 20°C per minute in an argon-

hydrogen atmosphere under continuous observation. The results showed that cracking had occurred between the eutectic nodules and denting at the triple points as in the case of commercial as-received Galfan. Thus the microstructure observed in commercially obtained Galfan has been recreated using Galfan alloy without a steel substrate as shown in Figure 10. Samples of polished as-received Galfan and directionally solidified Galfan ingot alloy have also been analyzed at Lehigh (see Figures 11a and 12a respectively). The lines shown represent the course of a series of analytical readings between 2 points. These lines are about 60 microns in length and analyses were carried out using an electron probe microanalyzer at distances of about every micron. Figures 11b and 12b show a series of traces for, lead, aluminium and zinc corresponding to Figures 11a and 12a respectively. These traces confirm the presence of high concentrations of lead at the edges of the primary dendrites and triple points. The lead levels obtained are about 0.3%, which represents a concentration of about 100 times that of the lead level in the homogeneous Galfan alloy.

It is perhaps not difficult to explain the presence of these lead particles between the eutectic nodules since owing to the limited solubility of lead in solid zinc aluminium alloy, the rejection of lead into the melt as the temperature falls would be expected. Thus the lead would be concentrated in the regions which solidify last.

It is now appropriate to consider whether the presence of increased lead concentration, or possibly any other impurity, could contribute to the tendency of the Galfan to produce dents or cracks.

It is known that from thermodynamic considerations that any impurity may effect the degree of undercooling and also the freezing range of the alloy. It is perhaps possible that in this case, as a result of the presence of high lead or other impurity concentrations that the eutectic nodule boundaries are being weakened and therefore may be more likely to rupture under the inevitable stress which is generated during solidification. It is the answers to these questions and others that Lehigh intends to find by continuing their work.

Summary

Microscopic examination of as-received Galfan samples has shown evidence of segregation, denting and cracking.

Experiments using polyethylene oxide have been carried out to model Galfan solidification. The model has demonstrated the importance of shrinkage during solidification with respect to the occurrence of cracking and denting.

It has been possible to relate solidification rate and microstructure using directional solidification. The presence of halos around aluminium rich primary dendrites suggest aluminium is a better nucleant of zinc than zinc is of

aluminium. Consequently, a zone of eutectic coupled growth has been assumed on the aluminium rich side of the eutectic composition.

Insitu solidification of Galfan alloy observed under the microscope has successfully simulated coating solidification in production. This has shown denting and cracking at nodule boundaries and triple points and the presence of lead at the nodule boundaries.

Many of the effects shown in this paper have been beautifully captured by Lehigh on video which is now available for viewing.

Further Work

Despite the undeniable high quality of this work and its undoubted significance, a greater level of industry support is required to ensure continuation.

If sufficient support is forthcoming the investigators intend to:

- Complete a literature survey of the background information.
- Complete the work on Galfan coating characterization.
- Continue a determination of the microstructural factors which are associated with denting in Galfan and identify the solidification conditions which control these factors.
- Produce Galfan sheet in the laboratory using selected dipping parameters to minimize denting.



Figure 1. Bright Field Image of GALFAN Coating Surface As-Received, Showing Grain Boundary Dents



Figure 2.

Scanning Electron Micrograph of GALFAN Coating Surface. Matching Edges indicate cracks rather than grain boundaries. Small bright particles on either side of boundary are impurities.



Figure 3. Schematic illustration of GALFAN development from a surface view.



Figure 4. GALFAN Cross-Section Showing Cracks and Primary Zinc (arrows).



Figure 5. Eutectic cell formation during the directional solidification of the GALFAN alloy.



Figure 6. Interlamellar spacing as a function of growth rate for the Zn-Al eutectic.



Figure 7. Cell spacing as a function of growth rate for the GALFAN alloy.



Figure 8. Zinc-rich halos (arrows) surrounding Al-rich dendrites in the GALFAN alloy.



Figure 9. Schematic illustration of the zone of coupled eutectic growth for the Zn-Al system



Figure 10.

Cracking at eutectic nodule junctions during the insitu solidification of the GALFAN alloy. Bright spots (arrows) are lead particles.



Figure 11a. Polished Galfan surface used for EPMA analysis. The line represents the analysis path, starting at "A" and ending at "B".



Figure 11b.

EPMA results for Zn, Al, and Pb. Note that the Pb spikes are associated with proeutectic dendrite edges (arrow #1 in Figure 11a) and eutectic nodule triple ponts (arrow #2 in Figure 11a).



Figure 12a. Directionally solidified GALFAN alloy. 1000x.



Figure 12b. Directionally solidified GALFAN alloy.

QUESTIONS AND ANSWERS

Dubois:	How many industrial samples have been looked at in this study?		
Stoneman:	I'm afraid I don't know the answer but I think it was a very limited number.		
Hoboh:	Do you know what the bath's lead composition was?		
Stoneman:	The lead content is given as 0.0029% wt.		
<u>Capul:</u>	Do you have plans to investigate whether magnesium has an affect on the eutectoid and whether can tie up the lead so that it is kept out of the grain boundaries?		
Stoneman:	I think the answer to that is yes because they do intend to look at tin, cerium, and other trace elements in the same ways as they have the lead. I notice that the magnesium content given for the alloy in this study is 0.002%.		
Dubois:	Have you seen any Ce or La concentration, even in the form of oxides?		
Stoneman:	The report does not indicate that they have.		
<u>Dubois:</u>	I will comment more on the compositions in my report tomorrow, but I think we have some problems with the analysis of Pb, Ce, La, etc. I am concerned that the compositions quoted in this paper and others is the right one because it is very difficult to get the actual content. I am sure that Pb will be an interesting element to look at to determine if we must reduce it. In case that is necessary, I am afraid we have some problems in analyzing it.		
Stoneman:	Considering what you just said, would you like to suggest what you think the Pb level might be?		

	<u>Dubois:</u>	No. My point is that we see the presence of Pb nodules here and given Pb composition but I'm not sure that the Pb you and others have report in other papers is the actual composition and whether we can ma comparisons of different reports. I notice in our own pot, the reported composition varies by a factor of 5 with no explanation. We use the sa alloy supplier, the same process, etc.	
	Leroy:	I would like to have more information concerning the correlation of Pb particles and cracking. Do you think Pb particles which are basically ductile could induce cracks or is it some other form of lead segregation in binary which could be responsible for the cracks as is common in steel? Phosphorus could induce embrittlement but no particles.	
	Stoneman:	I think the point here is that Lehigh observed that Pb nodules consistently appeared at all boundaries wherever there were cracks. They are not saying that the Pb is the cause of the crack but there appears to be a relationship and further investigation will almost certainly reveal worthwhile knowledge.	
	Leroy:	Does Lehigh plan to use Auger Spectroscopy to investigate the cell boundary?	
	Stoneman:	Yes	
•	Leroy:	That is good. I think this is a very important project for Galfan.	

Centre de Recherches

Centrum voor Research

Métallurgiques

in de Metallurgie

Association sans but lucratif

Vereniging zonder winstoogmerk

ILZRO PROJECT ZM-285

CONTINUOUS GALFAN COATING OF STEEL SHEET AND WIRE

Progress Report Nr 26

INDUSTRIAL GALFAN PRODUCT CHARACTERIZATION PROGAMME

First Interim Report Period January 92 - June 92

Project Leader: M.LAMBERIGTS, Head, Surface Science

Supervisor: V.LEROY, Director, Metals Science

Research sponsored by : International Lead Zinc Research Organization, Inc. 2525 Meridian Parkway P.O.Box 12036 Research Triangle Park, NC 27709-2036, USA

August 1992

INDUSTRIAL GALFAN PRODUCT CHARACTERIZATION PROGRAMME

Table of Contents

EXECUTIVE SUMMARY

1 INTRODUCTION	1
2 LICENSEES' RESPONSE	1
3 BASE MATERIAL PROCESSING ROUTES	3
4 CONTINUOUS ANNEALING	4
5 HDG PROCEDURES	5
6 FINISHING TREATMENTS	6
7 EVALUATION PROGRAMME	6
 8 RESULTS a) Organization b) Coating Chemistry c) Coating Weight d) Coating Roughness and Spangle 	8 8 8 10
9 CONCLUSIONS	11
APPENDIX 1 XRF Coating Thickness Evaluation	13
LIST OF REFERENCES	14
FIGURES 1 THRU 13	15

EXECUTIVE SUMMARY

The GALFAN Steering Committee recently decided that the work to be carried out during 1992 and beyond by CRM as part of ILZRO Project ZM-285 should essentially be devoted to characterizing industrial GALFAN products. The aim of the exercice is to establish that apparently different supplies are in fact equivalent in terms of user's properties.

CRM was then supplied with 23 GALFAN products and corresponding duly completed information forms from 11 steelmakers in Europe, Japan and the US. Based on their steel substrate chemistry, these products were segregated in two major materials groups (ELC and Ti-IF), although two additional categories were created to accomodate one high strength steel and one pseudo-rimming grade.

The evaluation work accomplished so far has emphasized substantial differences between the various processing routes involved, which were shown to reflect on many coating general properties.

During the next semester, those preliminary tests will be completed and global product user's properties will be evaluated.

> C.R.M. Surface of Metals

1.- INTRODUCTION

When the GALFAN Steering Committee last convened in Liège, Belgium, on January 22, 1992, its Members confirmed their previous decision¹ that the work to be carried out during 1992 and beyond by CRM as part of Project ZM-285 should essentially be devoted to characterizing industrial GALFAN products.

As a matter of fact, they had already learnt² that GALFAN suppliers are sometimes faced with their customers' uneasiness about a coating alloy which comes in differently processed distinct variants:

- a) Al contents have been reported to vary from 4.2% to 4.9%,
- b) some GALFANs may contain limited Si and/or Mg additions, while others do not,
- c) strip-bath temperature gaps may vary from less than 20°C to more than 100°C, and
- coating solidification rates span a very wide range, depending on line capability.

Their main concern was therefore to establish that apparently different current supplies are in fact equivalent in terms of user's properties.

At that time, active licensees had already been invited by ILZRO to take part in the programme and supply CRM with fully documented GALFAN sheet samples^{3,4} corresponding to 3 distinct steelgrades [CQ (Commercial Quality), ELC, and ULC-Ti], as hotdip coated according to their current practices and considered in the unpainted condition.

2.- LINCENSEES' RESPONSE

Over a five-month period extending from January 24, 1992 (Supplier Nr 2) to June 23, 1992 (Supplier Nr 4), CRM was supplied with 23 GALFAN products and corresponding duly completed information forms from 11 steelmakers in Europe, Japan and the US.

Notwithstanding their particular denominations which the steelmakers sometimes attribute to reflect global quality differences (CQ, ELC, DQSK, SPHC, ES, SI, IF,...), the steels involved can be segregated in 4 groups, based on their chemical compositions (Table 1).

Group	St.gr.	Supplier	Nat.	Th. (22)
1	ELC	1	1	1.00
_		2	1	0.75
		3	1	0.35
		4	1 1	0.80
		5	1	0.35
j		6	2	0.97
		7	1	0.39
		8	1	0.86
		9	1	0.60
		10	1 1	1.12
	,	- 11	1	0.80
2	ELC-PR*	1	1	1.5
3	ULC	10	1	1.45
4	ULC-IF	1	3	0.88 & 1
		2	1	2
		6	2	1.97
5	ULC-IF High Ti	6	2	0.97
6	C-Mn	1	1	0.97

*: Pseudo-rimming grade

Table 1: Steelgrade distribution

Corresponding composition ranges are defined herebelow:

	ELC	ELC-PR	ULC	ULC-1F	ULC-IF High Ti	C-Mn
с	36-60	26	6	1.9-4	9	157
S	1-20	10	17	4.2-12	8	14
Mn	37-330	194	230	89-219	195	929
P	6-20	20	6	8.4-16	13	14
Si	1-30	2	5	5-17	3	9
A 1	13-63	7	50	27-40	35	32
N	2.3-5.8	1.9	4.7	2.1-6.5	4	2.7
Ti	-	-	-	52-66	125	-

Table 2: Composition ranges (10⁻³%)

It must be noted that distinct materials sometimes originate in the same heat, and even in the same coil, and only differ from one another by their coating weights (modified line work conditions). This is particularly true for the 6 samples from supplier Nr 6 (2 ELC, 2 ULC-IF, and 2 ULC-IF High Ti), coming from 3 coils only. The differentiation will however prove quite beneficial to assess the effects of coating thickness and microstructure on product global quality.

Although apparently simple enough, the material ranking given above had to be further simplified in a first appoach for the preliminary evaluation work of this interim report: ELC, ELC-PR and Ti-free ULC were put thus together in the "ELC" family, while ULC-IF and ULC-IF High Ti were considered to belong to the same "IF" group.

Two distinct catergories have been maintained for the solitary C-Mn high strength steel and the pseudo-rimming grade, which is otherwise characterized by a typical ELC composition. Those two "singular" materials were excluded from the statistical tests detailed below.

However convenient at this introductory stage, steelgrade confounding certainly looks somewhat arbitrary, and it will be abandoned in future deeper individual evaluations.

3. - BASE MATERIAL PROCESSING ROUTES

Although the information has not been made available in all cases, hot-rolling finishing temperature seems to have been kept in a fairly narrow range (830-882°C) for all but one^a ELC grades, while coiling temperature varied from 540 to 735°C, which must have put the materials in definitely distinct micro-precipitation conditions.

On the other hand, IF grades were finish hot-rolled between 900 and 939°C, before being coiled beteen 600 and 689°C.

With only one exception^b, all materials were <u>cold-rolled</u> on tandem mills to a total reduction ranging from 40 to 87%. Rolling lubricants were extremely diversified: they were prepared either

⁸

 $T_f = 780$ °C; $T_c = 540$ °C Supplier Nr 11's 4-high reversible mill b

from simple tallow and mineral oils, or from commercial products (Croda, Quaker, Sphinx RL 201, United LT 8, ...).

As was already apparent from Table 1, steel gage was usually higher for IF grades than for their ELC counterparts. This is further evidenced by the top left diagram of Figure 1, which compares gage statistical distribution curves (suppliers' code numbers are listed along the curves)^c. This implies that care will have to be exercised when it comes to confronting ductility features pertaining to products of distinct substrate thicknesses.

4.- CONTINUOUS ANNEALING

Surface preparation was sometimes non-existent and sometimes involved either simple NONOX preheating or alkaline cleaning (spraying, brushing and electrolytic cleaning).

A variety of <u>furnaces</u> were used for continuous annealing [direct fire (DR), radiant tubes (RT), non-oxidizing furnaces $(NOF),...]^d$. Depending on the type considered, hydrogen concentration in the protective atmosphere and corresponding dew-point varied from 4.7 to 75%, and from -60 to -19°C.

Maximum <u>annealing</u> temperature was always comprised between 670 and 834°C for ELC grades, and between 820 and 850°C, for IF grades, with a soaking time of 12-55 sec and 30-65 sec, respectively.

In this connection, the top right diagram of Figure 1 compares maximum annealing temperature statistical distribution curves: it emphasizes the significant influences of both steelgrade and material origin. As expected, the former effect reflects IF steel higher recrystallization temperature, while the latter has more to do with local practice, which will certainly deserve further comments at a later stage.

Q(Steelgr) and Q(Supplier) respectively represent the significance thresholds of corresponding effects (ANO-VA or Kolmogorov-Smirnov tests): the lower the Q, the more significant the effect.
 MORE DE ADD DE DE CORDINATIONS were mentioned by sever

NOF-RT and DR-RT combinations were mentioned by several participants.

Although IF steels do not require any <u>overageing</u>, 3 out of 8 however undewent one, wherever line design made it inescapable (37-40 sec). Conversely, 11 out of 13 ELC grades were not submitted to one: this might have an effect on their ultimate ageing properties^e.

Beyond possible differences in equipment performance, <u>coo-</u> <u>ling</u> to metal dip temperature must obviously have been performed at a rate in direct relation with steel gage and line speed. Although the product characterization forms sometimes did not even mention it or often failed to give the temperature drop over which it was computed, thus making the information somewhat unreliable, cooling rate was often reported to lie in the 6.1- 20° C/sec range, for those cycles involving an overageing step, and between 2.5-60°C/sec, for the others.

Clearly enough, those wide cooling rate variation ranges may just reflect inconsistent computation methods, but they might also result from definitely distinct line capabilities. If necessary for the proper analysis of future results, suppliers will be requested by CRM to complete the information.

5.- HDG PROCEDURES

GALFAN <u>bath Al content</u> was reported to lie between 4.19 and 4.65%, the spelter being kept in the 418-488°C temperature range. The bar graph of Figure 1 compares the corresponding data as they were made available by the various suppliers (ELC and IF steelgrades only). Here again, differences in local practice are clearly evidenced.

Hot-dip processes could be segregated into two distinct groups, according as the metal-liquid bath <u>temperature gap</u> was either comprised between -5 and 48°C, or between 61 and 109°C. Obviously enough, the latter condition may have sometimes resulted from the characteristic cooling rate of a particular steel gage, but there are cases, where it clearly looks quite purposeful (Zinquench-like procedures). Significant differences between local ELC and IF hot-dip processes are illustrated by the three bar diagrams of Figure 2.

[•] Only suppliers 1 and 4 reported an overageing step prior to hot-dipping.

Line speed variations (between 21 and 165 m/min) might either reflect HDG line technical limitations (steel gage, furnace capability) or the steelmaker's desire to optimize annealing conditions (IF steels). It might also be strongly related to the <u>solidification rate</u> to be achieved with the existing cooling facility (air, air/water mixture, mist). Here again, though, incomplete information makes it very difficult to assess the reliability of the data (reported values in the 1.6-50 °C/sec range).

<u>Wiping gas</u> was either air (14 cases), nitrogen (8 cases), or some otherwise undefined "gas" (1 case); resulting <u>coating</u> <u>weights</u> can be split in two groups: between 92 and 141 g/m², and between 162.5 and 280^{f} g/m², thus only very imperfectly meeting the initially requested values (100 and 255 g/m²).

6.- FINISHING TREATMENTS

Except in two cases⁹, the GALFAN products under consideration received various degrees of skin-passing (from 0-2%) and/or stress-levelling (0-1.2%).

The bottom right diagram of Figure 2 suggests that skinpassing and stress-levelling total deformation control was purposefully better for IF grades than for their ELC counterparts, for which it extended from 0 to more than 2%. The diagram also emphasizes a significant origin effect [Q(supplier) < 10^{-4}].

Although it had specifically been requested that the materials be supplied in the unchromated, simply oiled condition, 11 out of 23 had effectively received some chromic rinse.

7. - EVALUATION PROGRAMME

In conformity with the initial programme, the evaluation work was assigned to CRM. It was decided that the following tests would be carried out, to assess the visual aspect and metallurgical features of the coating itself, together with the user's properties of the total product (Table 3).

Corresponding results will be correlated with the various

f One exceptional value at 305 g/m^2 .

g Supplier Nr 10's ELC grades.

product characteristics commented on above. Depending on the results, the success of this major piece of work might require that some suppliers complement the information they have already given.

Object	Gen. Feat.	Properties	Tests
Coating	Visual aspect	Roughness Spangle Denting	H-T T4000* FA-RLS** FA-RLS
	Phys. Prop.	Thickness Hardness Adhesion	Permeascopy XRF Dissolution Metallography Microhardness EIS ⁰ 00
	Metal. Prop.	Passivation Chemistry Microstructure	Sup. Al ₂ O ₃ [¢] Dissol.+AA ^{**} XRF SIMS Metallography
Product	Ductility	Galling Cracking Powdering	U-Bend Draw-Bead 2T-Bend T+SS ^o Cup-test
	Corrosion	Outdoor Accelerated Intercel.	Mod. Scab SS Wet corros.
	Weldability	Hoesch cont.	Spot weld.

*: Digital Hommel-Tester T4000

**: Fourier analysis of roughness linescan ASCII files

♦: Electrochemical Impedance Spectroscopy

⁰⁰: See "Ductility"

CRM method whereby soluble and total Al are determined separately

- ••: Combined chemical dissolution and atomic absorption
- •: Combined interrupted tension and salt spray test
- D: On selected materials only.

Table 3: Evaluation Test Schedule

8.- <u>RESULTS</u>

8.a.- Organization

A new special storing facility had to be installed at CRM to accommodate the numerous materials as they were arriving in packages, over 100 kg in typical weight. It is only in early May, when no additional receptions could reasonably be expected, that evaluation work actually started.

An internal number coding was then devised, and test-piece sampling and coding were made. The various CRM laboratories were supplied with whatever cut-to-dimension material they needed, so that testing could begin in the shortest delay.

8.b. - Coating Chemistry

A first round of chemical analyses focused on Zn, Al and Fe: La and Ce (ICP) will be determined at a later date.

Quite as expected, coating and bath Al contents tend to increase together, but the relation standard error of estimate is so high that the suggestion of process-associated secondary effects looks very strong indeed (Figure 3). If confirmed, these effects must induce differences in product quality consistency and justify distinctly adapted spelter management policies.

In this connection, the bar graphs of Figures 4 and 5 emphasize significant differences between GALFAN coatings from distinct origins, while suggesting substantial variations in coating-substrate reactivity, as it can be estimated by the amount of Fe in the coating. As matter of fact, interface intermetallics are essentially made of Fe-Al compounds, which makes unit surface Fe weight a good index for their abundance.

Although no clear statistical relationship has been established yet, it is very likely that coating chemistry variations are influenced in a very subtle way by dot-dip (metal-bath temperature gap,...) and coating solidiification conditions.

8.c. - Coating Weight

All suppliers provided their own total coating weight evaluations (2 sides), which they presumably derived from Reinhardt-
Anderson dissolutions. In order to avoid possible procedurerelated discrepancies and detect side by side coating differentiations, it was decided to confirm those results by further weight loss (Reinhardt-Anderson), chemical (total coating dissolution in HCl and subsequent solution chemical balance computation based on atomic absorption results), and physical (X-Ray Fluorescence, hereafter denoted by XRF, and permeascopy) methods.

Except for XRF, the above-mentioned procedures are all very familiar to those used to deal with coating thickness problems, whether it comes to basic principles or to capability limitations: therefore, they do not need any further comments.

The picture may be somewhat different for XRF, whereby the specimens are irradiated under an angle φ by a polychromatic X-Ray primary beam, which induces atoms in the coating and underlying substrate to fluoresce.

The fluorescence secondary beam, detected under an angle ψ , is made of distinct components, the wavelengths of which are characteristic of the various elements involved.

Corresponding intensities depend on coating thickness and elemental abundances, as described by the universally accepted linear absorption theory. In the present study, coating thicknesses were evaluated from Fe fluorescence attenuation measurements. Details are given in Appendix I, to help the reader appreciate the capability and limitations of the method.

Figure 6 compares suppliers' (2 sides) and corresponding CRM (accumulated sides) thickness data. It is clearly seen that CRM weight loss and chemistry measurements are in fairly good agreement with suppliers' weight loss results, although they tend to be slightly lower for thinner coatings. The global agreement is even better for XRF data, but individual result deviation looks somewhat higher, due to the limitations expounded in Appendix I.

Figures 7 and 8 pertain to each side and make it possible to compare the capabilities of the various methods used at CRM, while also providing more information on coating weight side differentiation.

They show that chemistry mesurements underestimate coating weights very slightly, because of elements (impurities) or compounds (undissolved oxides,...) which are not taken full account

of in the final chemical balance.

They also confirm the general agreement between weight loss and XRF results, although, for still unclarified reasons, the latter have not alway the same quality (compare Figures 7 and 8).

Finally, permeascopy looks the least robust method of all, inasmuch as its results get inadmissibly scattered for thicker coatings (Figure 8), or even do not relate properly with weight loss data (Figure 7).

8.d. - Coating Roughness and Spangle

As was mentioned in section 7 above, coating roughness was assessed from digital roughness files involving 8,000 measurements taken at regular intervals (every 6 μ m) along 48-mm long linescans. The equipment in-built data processing facility then automatically yields classical roughness features, among which the following were given particular attention:

- Rt: the maximum coating surface altitude variation along the linescan (in μ m),
- Rmax: the maximum peak-to-adjacent valley height difference (in µm),
- Ra: the average absolute altitude, as computed along the whole linescan (in μ m), and
- Rz-D: the "weighed" Rt value (in μ m), as averaged after the total linescan has been divided in five consecutive sections, thus lessening the effect of singular irregularities (scratches).

For the ELC-and IF-based products considered in this study, they vary substantially from supplier to supplier (Figure 9), while linear relations exist between them (Figure 10).

This suggests that all surface roughness features are similarly affected by the same process-associated effects. At this stage, it is very difficult to fully account for the observed variations, but some joint influence of metal-bath temperature drop, and skin-passing and stress-levelling total deformation can certainly be put forward, based on our current correlation analysis (Figure 11).

A roughness linescan can also be looked at as the superimposition of a short-range local roughness and a longer-range altitude variation more in relation with eutectic cell arrangement.

Local altitude Z(X) can then be approximated by:

$$Z(X) = A \cdot \sin \left(\frac{2\pi \cdot X}{\lambda} + \varphi\right) + \Delta Z$$

where A and λ respectively represent the basic amplitude and wavelength of the roughness "undulation" (also often called "waviness"). As was just suggested above, A is presumably related to cell boundary depletions, while λ has more to do with cell mean intercept, thus giving access to some degree of spangle quantification.

In the same connection, λ and ΔZ are the wave phase angle (depending on the linescan origin) and unaccounted for local altitude variations: clearly enough, these two parameters are then of lesser importance for the comments below.

Having said that, it must be appreciated that the waviness features defined above were derived from major size curve fitting computations (8,000 points involved in each linescan) carried out on far from purely periodic profiles: some "sub-periodicity" is actually the best one can expect from them.

Consequently, corresponding correlation coefficients were always very low (R < 0.35), and care should certainly be exercised when commenting on A and λ values. Furthermore, the extreme smoothness of some roughness profiles can lead the curve fitting computations to yield an abnormally long wavelength.

Despite all these limitations, basic amplitudes and wavelengths show the same origin dependence as classical roughness features (Figure 12). Furthermore, they relate sensibly with the latter: basic amplitude A increases parabolically with Rmax, while amplitude-to-basic wavelength ratio A/λ is in direct relation with Ra (Figure 13).

9.- <u>CONCLUSIONS</u>

The industrial GALFAN product characterization programme constituting the major part of ILZRO Project ZM-285 for 1992 and beyond is now well underway. Over a five-month period extending from January 24, 1992 to June 23, 1992, CRM was supplied with 23 GALFAN products and corresponding duly completed information forms from 11 steelmakers in Europe, Japan and the US.

Based on their steel base chemistry, those products were segregated in two major material groups (ELC and Ti-IF), two additional categories having however been created to accomodate one high strength steel (HS) and one pseudo-rimming ELC grade.

Most of the work accomplished so far was aimed at characterizing the materials, based on the information provided by the suppliers and CRM confirmation tests.

Substantial differences were thus identified between the various processing routes involved, which were shown to reflect on many coating general features (chemistry, thickness, roughness and spangle).

During the second semester of 1992, those preliminary tests will be completed and global product properties (ductility, corrosion resistance,...) will be assessed according to initial plans. Depending on the results, some of the participating suppliers will be invited to complement the information they have already provided.

APPENDIX 1

XRF Coating Thickness Evaluation

If I and I₀ respectively represent the Fe fluorescence intensities obtained before and after coating removal (coating thickness th and specific gravity ρ), and assuming that μ_p and μ_f are the absorption coefficients pertaining to the primary and fluorescence beams, the generally acknowledged GALFAN non-reactivity (Fe fluorescence entirely originates in the substrate) allows to apply the linear absorption theory as follows:

$$\frac{I_{th}}{I_0} = \exp\left[-th \cdot \left(\frac{\mu_p}{\sin\varphi} + \frac{\mu_f}{\sin\psi}\right)\right]$$

or, even better, if CW is the unit surface coating weight (in g/m^2):

$$\frac{I_{th}}{I_0} = \exp\left[-CW \cdot \left(\frac{\mu_p}{\rho \cdot \sin\phi} + \frac{\mu_f}{\rho \cdot \sin\psi}\right)\right]$$

which leads to:

$$CW (g/m^2) = - \frac{\ln \left(\frac{I_{th}}{I_o}\right)}{\frac{(\frac{\mu}{P})}{\sin \varphi} + \frac{(\frac{\overline{\mu}_f}{P})}{\sin \psi}}$$

Specific absorption coefficients are documented for many metals, and those of Zn-Al-Fe alloys can be derived from their compositions as follows:

$$\left(\frac{\mu}{\rho}\right)_{alloy} = (\$2n) \cdot \left(\frac{\mu}{\rho}\right)_{2n} + (\$Al) \cdot \left(\frac{\mu}{\rho}\right)_{Al} + (\$Fe) \cdot \left(\frac{\mu}{\rho}\right)_{Fe}$$

Coating thicknesses can therefore be computed from Fe fluorescence attenuation measurements (I_{th}/I_0) , as soon as the coating chemistry and unit arrangement (φ , $\overline{\Psi}$) are known.

Quite obviously, characteristic μ/ρ values are wavelengthdependent, which makes it very difficult to accurately compute polychromatic primary beam absorption. As a first approximation, the elemental specific absorption coefficients used in this study were those pertaining to the $Co_{K\alpha}$ X radiation: if necessary, computations may be refined in the future. In spite of the limitations suggested above, XRF coating thickness evaluations present the advantage of characterizing 1 side at a time, over a reasonable surface area ($\phi = 45$ mm).

. .

LIST OF REFERENCES

- 1. GALFAN Steering Committee Meeting, CRM, Liège, Belgium, Monday June 10, 1991.
- 2. "Commercial GALFAN Quality Assessment and Solidification Control", CRM research work proposal for 1992, M.Lamberigts and V.Leroy, July 1991.
- 3. John L.Hostetler's GTRC letter of 6 November 1991 to Hoesch Stahl, Kawasaki, NKK Corporation, Nisshin Steel, Phenix, Rautarruukki, Sollac, Sumitomo, Thyssen, Voest-Alpine, Weirton, Wheeling Pittsburgh and Yodogawa.
- 4. John L.Hostetler's notice to all participating GALFAN sheet licensees of January 15, 1992.











Industrial GALFAN Characterization



Fig. 4.

Coating Composition Control









350



Industrial GALFAN Characterization



Coating Weight Control

Fig. 8.





II-30

Relations between Coating Roughness Features





Fig. 12.

Effect of Origin on Basic Roughness Features



SECTION II APPENDIX

QUESTIONS AND ANSWERS

<u>Capul:</u>	Did any of the sample sources report more than 4.8% aluminum in the GALFAN bath?
Leroy:	Yes. One sample. Data from two samples are missing in this report; one having a low Al content and one having a high content.
Dubois:	Is the Al content you have given the <u>effective</u> content?
Leroy:	I don't know. The contents shown were given by the supplier.
Dubois:	Did you also get the iron content? I think this should also be included in the report because we know the Fe is not normally soluble when the Al content is high.
Leroy:	We did receive the Fe content for each sample. We reported the total Al.
Dubois:	What method did you use to analyze the Al in the coating? I'm mainly concerned about pickling the specimen. Union Miniere will report tomorrow on some experiments with the pickling to see the effect upon the final results.
Leroy:	We have used the weigh-strip-weigh, x-ray fluorescence and permeascopy methods for determining coating thickness with good correlation between the methods and to the supplier data.
<u>Dubois:</u>	But how did you then analyze the coating composition? Did you use XRF? The accuracy would be like 1%. The reason I am so concerned about this is that we know there is some Al sticking to the steel in the form of some Fe-Al compound which nobody seems to know what it is but I expect the amount of Al in this layer is quite large and if the pickling is not good enough it could affect the Al analysis in the coating.

Section II— Appendix (cont'd.)

Leroy:	I repeat: there is good correlation of the coating analysis between the supplier and CRM. Now, the correlation of the coating composition and the bath composition is not so good. Here we may have a problem.
<u>Chairman:</u>	Here again we see the importance of developing an accurate and reliable standardized method for obtaining a bath sample.
<u>Dubois:</u>	Concerning waviness. Do you know if the samples not temper rolled (skin passed) were leveled? You know that in leveling the leuter lines are very closely spaced and this might affect the measured waviness.
Leroy:	We do have this data but we must clarify.
<u>Chairman:</u>	I am sure we will find future Progress Reports very interesting and this program will discover many things concerning the effect of coating line processes on the various evaluations and characterizations of the coating.

-

Corrosion Resistance of Unpainted GALFAN Steel

Abstract

The paper first summarizes the corrosion mechanism of Galfan as reported by CRM in Progress Report No.24 for ILZRO project ZM-285 and compares it to the mechanism of regular galvanizing. It then compares and evaluates long term exposure corrosion of Galfan as reported by N.V.Bekaert Co., C.R.M., New Zealand Steel and Nisshin Steel to demonstrate Galfan's unusual parabolic corrosion rate. Finally, it correlates the Nisshin Steel data from rural, industrial and marine exposures to years to appearance of red rust and to years of useful life so that realistic life costs for Galfan can be compared to regular galvanizing.

© 1992 Galfan Technical Resource Center

John L. Hostetler, P.E., Director, Galfan Technical Resource Center International Lead Zinc Research Organization Research Triangle Park, NC, USA

Foreword

Acceptance of Galfan ® has grown rapidly in Japan and Europe; it is now underway in North America and is just being introduced into South America and the rest of Asia.

Approximately one-half of the worldwide Galfan production has been in the form of prepainted sheet as it is used in architectural, appliance and automotive applications. The rest is in unpainted sheet, wire, small diameter tube and small parts.

Galfan is an *improved* galvanizing alloy which offers three major improvements over other galvanizing alloys, namely:

Corrosion Resistance, Formability, and Paintability

Each of these attributes are discussed in a booklet such as this one which is first in the series. GTRC recognized the need to translate the wealth of scientific knowledge gained from extensive Galfan research into a discussion of the commercial benefits resulting from theses attributes.

This booklet is therefore, directed more toward those who are involved with designing, specifying, marketing or selling Galfan than to scientists researching it. It contains information which can be used for developing comparisons for years of life, years to appearance of red rust and for owning costs.

The Author acknowledges that the research data referenced herein is not his own and that not all references are listed because the paper's purpose is not primarily to disclose scientific discoveries, but rather to use them for arriving at the commercial benefits of Galfan.

Corrosion Resistance of Unpainted Galfan Steel

PART ONE THE CORROSION MECHANISM

Introduction

GALFAN is a significantly *improved* galvanizing alloy which can be used to protect steel in many architectural, appliance, agricultural, automotive and construction related applications. Experience and research indicates Galfan offers three distinctive areas of improvement when compared to regular galvanizing. They are:

- Corrosion resistance
- Formability
- Paintability

Any one of these improvements by itself might easily justify choosing Galfan but combining two or all three clearly makes it superior. This paper illustrates the *corrosion* performance of unpainted Galfan as it is typically used in outdoor rural, industrial and marine exposures.

Purpose of This Paper

The factors which influence the corrosion rate of Galfan as compared to regular galvanize make any effort to compare years of life in a given environment difficult but since we now understand the corrosion mechanisms and have accumulated longer term exposure results, correlations are accurate enough to be useful in making decisions for buying, specifying, and planning. That is the purpose of this paper.

Part One discusses corrosion mechanisms and presents evidence to show Galfan is a technologically improved galvanizing alloy. Part Two then shows how the improved corrosion resistance can be used to improve the *value* of galvanized products.

What is Galfan ?

Galfan is the patented binary alloy of zinc and aluminum at the eutectic ratio (95% Zn and 5% Al) which is now used for galvanizing sheet, tube and wire by almost 50 licensed Galfan producers throughout the world. It is not only the lowest melting temperature ratio galvanizing alloy, it is also the most formable and paintable and has more corrosion resistance than zinc alone. Its high purity requires that small amounts of rare earth mischmetals be added to increase its wetting power, preventing the occurrence of bare spots in the hot-dip coating process.

What is Galfan Steel ?

Galvanized steel is a generic term used to describe steel which has been coated with zinc or a zinc alloy. If the particular zinc alloy is Galfan, the galvanized steel is called **Galfan** steel. It is well known that a galvanized coating corrodes much slower than steel so it first protects the steel it covers by keeping corrosive elements away from the steel, acting as a *passive* barrier. A galvanized coating's special feature however, is its *cathodic* (or sacrificial) characteristic which means that even if it is cut, scratched or abraded away, the galvanize coating adjacent to the exposed steel will corrode first instead of the exposed steel.

Aluminum corrodes more slowly than zinc in most atmospheres so it is a better passive barrier but it cannot contribute adequately to the cathodic or sacrificial protection. *Galfan combines the strengths of both zinc and aluminum*, giving better *passive* barrier protection than regular galvanizing and better *sacrificial* protection than alloys having a lower zinc composition.

This paper describes the improved performance and lower cost of Galfan steel when used in exposed sheet applications such as roofing, siding, highway guard rails, culverts, noise abatement panels, etc. The same improved performance is also seen in Galfan wire and tube.

Corrosion Mechanisms

The corrosion mechanisms of galvanizing alloys must be understood in order to understand why Galfan's performance is improved. This can be done by reviewing the evaluations, characterizations and testing already reported in scientific and technical papers by other investigators and available from ILZRO.

Regular Galvanizing's Corrosion Mechanism

Regular all-zinc galvanized coatings corrode by dissolving and re-precipitating as zinc oxide crystals over the surface, thus the surface attains an irregular appearance as shown by a scanning electron microscope (SEM) examination of an exposed regular galvanized surface (*Fig 1*).

The corrosion products of zinc are $Zn(OH)_2$, ZnO (dehydration of $Zn(OH)_2$) and basic salts formed as a result of compounding $Zn(OH)_2$ with $ZnCl_2$ or $ZnCO_3$. The zinc oxides are porous and so allow free access of corrosive electrolytes to the zinc coating. This mechanism usually creates preferential pathways through areas of higher porosity to cause locally accelerated corrosion.

Galfan's Corrosion Mechanism

The SEM examination in Fig 2. of a corroded Galfan surface shows it to be much smoother. This is due to the lower reactivity of the eutectic microstructure which produces less of the porous corrosion products. A cross-sectional SEM examination of the typical Galfan eutectic/two-phase microstructure is shown in Fig 3.

Zinc corrosion in this case must follow the random directions of the thin parallel plates or *lamellae* in the microstructure. As the surface corrodes, albeit more slowly than regular galvanized, it leaves behind a surface of dense corrosion products richer in aluminum and therefore more passive and corrosion-resistant than regular galvanized.

Corrosion will be slowest when the lamellae are parallel to the sheet but even random oriented lamellae greatly reduces the rate of corrosion. Weight loss data and detailed studies of the microstructure described herein conclusively show two improvements in the Galfan mechanism:

- 1. The general corrosion rate is significantly lower then regular galvanized.
- 2. Galfan corrodes uniformly by dissolution of the sub-micron lamallae rather than along larger preferential pathways as in regular galvanized.

Even though there is not enough time for Galfan to develop its maximum passivity in short term tests, its slower dissolution rate is seen in accelerated corrosion such as salt spray tests and SO₂ cycle tests. Salt spray tests give a relative rating of the coating's behavior in a marine environment; the SO₂ cycle test indicates behavior in a heavy industrial environment

These relationships are complicated somewhat in atmospheres where both chlorides and oxides of sulfur are present because interactions can occur; sometimes one factor influencing corrosion can cancel out the effect of another.

Galfan's Unusual Corrosion Rate

A unique characteristic of Galfan actually *improves* its performance over time. Because regular galvanizing's rate of corrosion is essentially linear, it was first assumed that Galfan's would be too. Long-term testing by Centre de Recherches Metallurgiques, New Zealand Steel, Nisshin Steel and N.V.Bekaert however, all show that Galfan's rate of corrosion is parabolic rather than linear. These tests show Galfan's weight loss during the first two or three years to be only slightly less than regular galvanizing but as its surface passivates with time, its weight loss per unit of time decreases parabolically.

New Zealand Steel's tests were done at Manukau Heads, a high fog severe marine environment. They show that Galfan's coating thickness loss is not dependent upon the initial thickness (as it is in the case of regular galvanized) and that Galfan's loss is more uniform across the panel than regular galvanize. Figure 4 shows the comparison of the weight loss vs. time for regular galvanized and Galfan.

C.R.M.'s 5-year exposure tests are summarized in *Table One* and photographs of the test panels are shown in *Figs. 5a* to 5d.

CRM Fiv	e-Year Outdoo	or Corrosion '	Test
COATIN	IG THICKNES	S LOSS, micr	ons
Exposure Atmosphere	Regular Galvanized	GALFAN	Ratio
Rural Industrial Marine	10.4 15.0 20.0	3.4 5.4 10.4	3.1:1 2.8:1 1.9:1

TABLE ONE

The Bekaert tests shown in *Table Two* were conducted using steel wire rather than sheet but are shown here to demonstrate that this corrosion mechanism is a characteristic of the Galfan coating, not the substrate steel.

TABLE	TWO
--------------	-----

Corrosion	Corrosion Rates from Bekaert Tests		
WEIGHT LOSS (g/m ²) P	'ER 100 HRS. ASTN	A B117 SALT SPRAY	
Condition and Coating	Initial Rate up to (Hrs)	Final Rate to red rust (hrs)	
As-coated: Regular galvanize Galfan	57 (300) 28 (670)	24 (625) 9 (1150)	
Redrawn Regular galvanize Galfan	127 28 (320)	127 (150) 10 (600)	

When Nisshin's seven year exposure tests in rural, industrial and marine environments are shown graphically as in *Figs.* δa , δb and δc , it is easy to visualize the lower parabolic corrosion rate of Galfan as compared to the near linear rate of regular galvanized. Figure 7 shows X-ray diffraction examinations of the regular galvanized and the Galfan surfaces after five years of exposure in Nisshin's test's marine atmosphere.

An explanation for this characteristic is reported in CRM's Project ZM-285 Progress Report 24 in which two different coated steel substrates (IF and ELC) were investigated for corrosion mechanisms. This paper will deal only with the ELC specimen because the differences are significant only if the Galfan is to be prepainted. The substrate is further described in Table Three.

С	.032 %	Yield Strength	43,500 psi
Mn	.20	Tensile	52,900 psi
Si	.006	Elongation	35.9%
Ρ	.013	Coating Thickness:	
S	.014	Side 1	24.5 microns
N,	.0028	Side 2	21.7 microns

TABLE THREE

Galfan Characterization

The difference between Galfan and other galvanizing alloys is seen in the microstructures. Regular galvanizing alloys are essentially all-zinc which freezes into a single-phase microstructure, forming areas of different crystal orientation that are seen on the surface as "spangles". Al-Zn alloys such as Galvalume form two-phase microstructures in which aluminum phases are surrounded by the lower freezing temperature zinc. Galfan however, forms a hypoeutectic microstructure in which the zinc and aluminum freeze into cells of thin parallel plates called *lamellae*, together with some relatively small zinc globules. If the freezing rate is increased adequately, the microstructure can be made to be wholly lamellar.

Galfan's Initial Condition

Galfan's smooth surface is seen in *Figure 8* which shows an SEM evaluation of a typical initial uncorroded surface clearly showing a predominantly lamallar eutectic cellular structure with distinct orientations of adjoining cells.

The Scanning Auger Microprobe (SAM) analysis allows us to define Galfan's uncorroded alloying element distribution as shown in *Figure 9*. The SEM micrograph in the upper left corner and the in-depth chemistry images for Zn, Al, Mg, O and C are taken from the same area. The brighter the Auger images, the richer the element composition. The analysis shown in the top row of images was taken at a depth Z of 0.2 nm, which in effect measures the compositions of elements on the surface of the coating. It is clear that initially the top layer of the Galfan coating is a continuous aluminum oxide film. This aluminum oxide is created by high temperature oxidation formed during the hot-dipping process and is referred to as the thermal oxide.

Controlled ion sputtering can be used to see deeper into the coating, allowing changes in chemistry at various depths to be measured. The second and third rows of Auger distribution in *Fig. 9* show that the thermal oxide film is very thin, it disappears at 3 nm, where zinc clearly becomes the predominant element. It can also be seen that while Al is effectively present everywhere, it congregates in oxidized cell boundaries where no Zn is detected.

The bar graph in *Fig. 10a* compares the SAM analyses made at a depth of 0.2 nm at three precise locations, inside Zn-rich and Al-rich areas of the coating and at the cell boundaries. The tightly focused electron beam under-estimates oxygen concentrations and is subject to other errors and should, therefore, be considered a qualitative display only. Its main purpose is to confirm the concentration of Al in the cell boundaries. *Figure 10b* shows the chemistry profile of the Galfan coating to a depth of 7 nm. Al and Zn atom concentrations gradually return to their nominal values as the oxides disappear.

Galfan's Corroded Conditions

A similar analysis was made on coatings after exposure in a humidity cabinet for thirty (30) days. The SEM micrograph and X-ray distribution images of *Fig. 11* show intercellular corrosion (deep oxygen penetration along Al-rich boundaries).

The bar diagrams in Figure 12 give the local SAM analysis of corroded and noncorroded areas at 0.2, 3 and 60 nm below the surface. Although oxygen seems to be generally present in the top layer, Fig. 13 shows it is significant at the 60 nm layer only in the Al-rich areas. Figure 13 also shows that the uncorroded areas still have their thermal oxide film whereas corroded areas are covered with a thin zinc oxide-hydroxide layer at 3 nm, but with aluminum hydroxide below. Figs. 13 and 14 show carbon enrichment at the surface which is evidence of probable carbonate formations which are even less soluble than the hydroxides.

Intercellular corrosion results from the corrosion of the Al-rich cell boundaries when the electrolyte (containing oxygen) seeps in from the surface where it was formed. The Al-Zn hydroxides thus formed are pushed out of the cell boundaries by volume expansion and collect on the surface's thermal oxides. When this liquid dries, the Al hydroxide solidifies first; the Zn hydroxide collects on the top, producing the very thin Zn-enriched top cover.

Conclusions

- 1. Galfan's resistance to corrosion is more effective than regular galvanized because:
 - (a) Its thermal oxides of aluminum at the surface are more stable and provide a slower corroding, more *passive* barrier.
 - (b) Surface zinc corrodes first, leaving an aluminum-rich composition which is much more passive than regular galvanized.
 - (c) Its surface by-products of corrosion are less porous and not as prone to local corrosion.
 - (d) Its eutectic microstructure has a lower reactivity than regular galvanized microstructure, thus slowing its rate of corrosion.
- 2. Part One of this paper has introduced the scientific data and explanations to show there are differences in the rate of corrosion when comparing Galfan and regular galvanizing in various atmospheres. Part Two will show how this difference results in lengthening the life of the galvanized product or to reduce its cost.
- 3. Four long-term exposure studies conducted in different parts of the world (Belgium, New Zealand, and Japan) are reasonably correlated. All show the parabolic corrosion of Galfan and a near-linear corrosion of regular galvanized.



Fig. 1, Surface SEM Regular Galvanize surface after one year in a severe marine outdoor exposure (800X)



Fig. 3, Cross section SEM examination of GALFAN coating after one year in a marine outdoor exposure (3000X)



Fig. 2, Surface SEM GALFAN surface after three years in an industrial outdoor exposure (2000X)



Fig. 4, Coating thickness loss in marine environment New Zealand Steel Study



Fig. 5a Rural Atmosphere




Fig. 5c Marine Atmosphere

COMPARISON OF COATING THICKNESS LOSS FOR REGULAR GALVANIZE AND GALFAN

Nisshin Steel Co. 7 Year Exposure Study



CORROSION PRODUCTS FORMED ON REGULAR GALVANIZED AN GALFAN AFTER 5 YEARS EXPOSURE IN MARINE ATMOSPHERE



Fig. 7a Regular Galvanized



Fig. 8 UNCORRODED GALFAN SURFACE

ON IF STEEL

ON ELC S



Fig. 9 EXAMINATION OF UNCORRODED GALFAN

SEM Evaluation and Auger Spectrometry



Fig. 10 EXAMINATION OF UNCORRODED GALFAN SURFACE



10a Unexposed GALFAN eutectic cell compostion at 0.2 nm.



10b SAM evaluation of uncorroded GALFAN composition vs. depth.

Fig. 11

SEM and X-ray diffraction evaluation of cross section of GALFAN coating after 30 days wet corrosion test.





Fig. 12 CORRODED GALFAN SURFACE CHEMISTRY









Fig. 12d

Fig. 13 EXAMINATION OF CORRODED GALFAN SEM Evaluation and Auger Spectrometry



Fig. 14 SAM Evaluation of Corroded GALFAN Composition vs. Depth



Corrosion Resistance of Unpainted Galfan Steel

PART TWO THE PERFORMANCE ADVANTAGE

Benefits of Improved Corrosion Resistance

Because Galfan[®] corrodes more slowly than regular galvanizing, the first advantage which becomes apparent is that, given the same coating thickness, *the life of Galfan steel* will be longer than regular galvanized steels.

This feature of longer life results in fewer replacements which benefits the buyer, the infrastructure, and the ecology because:

- Users too often wait until the product has gone beyond its intended or useful life before replacing it. This may result in many kinds of failure, some of which may be risks to safety, consequential liabilities or damages, etc. If Galfan is used, there will be fewer failures, thus fewer consequences;
- 2. In an inflationary economy, each replacement will cost more than the original or the previous replacement. The *total cost* to replace the product must also include the cost to remove and dispose of the old;
- 3. Replacing a product often results in costly damage to other materials adjacent to or attached to it;
- 4. A replacement unnecessarily reduces the supply of the raw material resources; and

5. Eliminating a replacement conserves energy, reduces the cost of recycling and the hazard of disposal.

Galfan Performance

In a Nisshin Steel Corp. study, panels of regular galvanized steel and Galfan galvanized steel were exposed for 7 years to outdoor atmospheres in rural, industrial, and marine sites with results reported in Part One of this paper. Extrapolation of that data is seen in Table One and in the graphs in Figures 1a, 1b, and 1c.

The Japan Construction Center (affiliated with the Ministry of Construction) recently certified to manufacturers of pre-fabricated homes that:

"Galtite (Nisshin's Galfan) has two times better outdoor corrosion resistance than conventional galvanized of the same coating weight."

The evidence that Galfan has *twice the corrosion resistance* of regular galvanize is the same as saying Galfan galvanized steel has *twice the life* of regular galvanized steel. Actually, the 2:1 ratio is conservative. Table 1 shows the 15-year performance (extrapolated from the Nisshin 7 year results) ratio of Galfan to regular galvanize in three environments: rural, industrial, and marine, to be 2.4, 2.7, and 2.5, respectively. *The longer the exposure time, the better the performance ratio becomes.*

	Γ	otal Co	ating Th	ickness	Loss, mi	icrons	
			Yea	rs Exposi	ıre		
Exposure	5	*		/*		15**	
Туре	Regular		Regular		Regular		
Atmosphere	Galvanize	Galfan	Galvanize	Galfan	Galvanize	<u>Galfan</u>	Ratio
RURAL	7.6	4.8	10.0	5.4	18.8	7.8	2.4
INDUSTRIAL	12.7	7.8	16.6	8.0	31.6	11.7	2.7
MARINE	15.5	8.8	20.7	10.5	39.9	16.0	2.5

TABLE ONE

* Actual Nisshin Steel Data

** Extrapolated Data

Useful Life vs. Red Rust

Another characteristic of Galfan which leads to longer useful life compared to regular galvanized is the *effectiveness* of its coating thickness to resist the appearance of red rust. This characteristic is significant because in many cases the product should be replaced when unsightly red rust appears, even if the base steel is not yet affected (useful life). Red rust may show through a regular galvanized coating as thick as 8-12 microns whereas red rust does not show through Galfan until it is less than 1 to 3 microns thick.

The explanation for this is that the iron in the relatively thick $(5-15 \mu m)$ Fe-Zn binary alloy layer normal for regular galvanize is the contributor. In contrast, Galfan's intermetallic is very thin $(1 \mu m)$ and is composed of a ternary Fe-Al-Zn compound. Thus, Galfan's intermetallic does not contribute to rust formation.

The N.V. Bekaert Co., a Galfan galvanized wire producer in Belgium, found in comparing Galfan and regular galvanized wire that 1 μ m of Galfan did the work of 6 μ m of regular galvanizing because red rust appeared on the regular galvanize wire with 6 microns of coating still left, whereas red rust did not appear on the Galfan wire until the coating thickness was reduced to 1 micron as shown in Table 2.

USABLE COATINGS TO RED RUST								
Coating Thickness, microns								
Туре	Alloy	Free	Total	at 5%				
Galvanizing	layer	coating	original	red rust				
Regular	3	25	28	6				
Galfan	2	20	22	1				

TABLE TWO

Thus, in this case a 20 micron thick coating of regular galvanize may show red rust after losing only 14 μ m of thickness whereas Galfan's already slower corroding coating of the same initial thickness can lose 19 μ m before showing red rust.

It should be noted here that Galfan wire is first hot-dipped in a regular galvanizing bath which forms the classic alloy layer. It is then hot-dipped in a Galfan bath in which Galfan's aluminum transforms the binary Fe-Zn alloy layer into a thinner ternary Al-Fe-Zn intermetallic. Nevertheless, there is even more intermetallic than would be found from a single dip process such as used for sheet or tubing.

Table Three shows the galvanized steel's useful life (until base steel is affected by loss of coating) in years of exposure and Table Four shows years of exposure until the appearance of red rust. The Tables are based on the graphic data shown in Figures 1a, 1b, and 1c with red rust showing at $8\mu m$ of regular galvanize, or $3\mu m$ of Galfan.

Buying and Specifying Issues

Therefor the issue confronting the *specifier*, *designer* or *buyer* of a galvanized product now becomes one of how to most effectively *take advantage* of the improved corrosion resistance of Galfan for the particular application and circumstances.

The issue confronting the *galvanizer* is whether or not he will incorporate the improvements of Galfan galvanizing into his galvanized product so that both *he and his customers* benefit.

Tables Three and Four show the dramatic increase in the years of useful life for Galfan steel or to the appearance of red rust as compared to regular galvanized. It makes the Galfan the Galfan product worth more ... gives it greater value. The Specifier designs more life into the Owner's asset, the Producer provides a significant improvement for his customer and the Buyer gets more for his money.

Value

The first consideration is value. The use of galvanized steel is so broad and varied that it is difficult to select an average or typical application to use as an example. Any cost analysis is complicated by the broad range in costs of the compared products.

There are however, computerized programs available through regional Galfan Development Associations or Galfan Licensees which can determine the savings possible by using a Galfan thickness equal to regular galvanized. Programs are available for (a) corrugated or profiled roofing or siding, (b) noise abatement panels, (c) wire fence, (d) highway guard rail and (e) culvert. The savings are significant for the individual User and for aggregate communities such as municipalities, countries, etc.

Galfan coated products such as corrugated roofing and siding, highway guard rail and culvert, agricultural and institutional fence or wire rope are dramatically increased in value because they can last two to four times as long as regular galvanized. The difference in the User's cost to replace the product alone is considerable when considering the life of the building, highway or structure. Additionally, there are other costs which should be considered:

- ... Escalation in price for the replacement
- ... Transporting and handling the replaced and the replacement
- ... Labor to remove the replaced
- ... Disposal of the replaced
- ... Labor to install the replacement
- ... Allowance for damage to adjacent materials
- ... Cost of new fasteners, attachment, etc.

Considering these additional costs, the *total cost for owning* the product may easily be 2 to 5 times the savings for the product itself.

The corollary of the value found in Galfan's longer life for an equal thickness of regular galvanized is *comparable life for a lesser Galfan thickness*. Whereas Tables Three and Four compare the years of life or years to the appearance of red rust for given coating weights of regular galvanized and Galfan, Tables Five and Six compare the coating weights of regular galvanized and Galfan required for given years of useful life or years to the appearance of red rust.

There are advantages to using only the thickness needed. They include:

- ... Improved surface appearance
- ... Lower cost
- ... Easier recycling or disposal
- ... Conservation of essential resources

In some applications such as floor decking, the coating needs only to protect the steel or prevent rust until it is covered with another non-corrosive material. In such cases, a given thickness of Galfan can provide performance equal to more than twice the thickness of regular galvanized.

CONCLUSIONS

Galfan's improved corrosion resistance creates benefits for the producer, the user, the environment, and even a country's economy.

Reasonably accurate forecasts of the savings in the life cycle of a building or product can be computed when the corrosion rates of the compared coatings are known. Nisshin Steel's seven year exposure studies can be extrapolated to find those corrosion rates and thus, the life of regular galvanize and Galfan coatings in rural, industrial, and marine atmospheres.

Conversely, a Galfan coating thickness can be found which will provide specified years of useful life or years to appearance of red rust.

GALFAN TECHNICAL RESOURCE CENTER

Research Triangle Park, NC, USA

			YE	CARS	OF US	EFUL	, LIFE	*			
Type Coating	Two-side Coating Mass, g/m2										
and Atmosphere	100	185	200	275	350	450	500	600	750	1000	
Regular Galvanize											
Thickness, microns	7.0	13.0	14.0	19.3	24.5	31.5	35.0	42.0	52.5	70.0	
Rural	4.5	9.6	10.5	15.5	20.8	28.3	32.2	40.2	52.7		
Industrial	2.6	5.3	5.8	8.4	11.1	14.9	16.9	20.9	27.1	37.9	
Marine	2.0	4.0		6.4	8.5	11.3	12.8	15.8		28.6	
	1										
Galfan	1										
Thickness, microns	7.6	14.0	15.2	20.8	26.5	34.1	37.9	45.5	56.8	75.8	
Rural	13	32	35	51							
Industrial	5	21	24	38	52						
Marine	5	12	14	22	30	41	46				

TABLE THREE

TABLE FOUR

	YEARS TO RED RUST APPEARANCE*									
Type Coating				Two-si	ide Coatin	ng Mass,	g/m2			
and Atmosphere	100	185	200	275	350	450	500	600	750	1000
Regular Galvanize Thickness, microns	7.0	13.0	14.0	19.3	24.5	31.5	35.0	42.0	52.5	70.0
Rural Industrial Marine	NR NR NR	3.0 1.7 1.3	3.7 2.1 1.7	8.1 4.5 3.4	12.9 7.0 5.3	19.8 10.6 8.1	23.4 12.5 9.5	31.0 16.3 12.4	43.1 22.3 16.9	32.9 24.8
Galfan Thickness, microns	7.6	14.0	15.2	20.8	26.5	34.1	37.9	45.5	56.8	75.8
Rural Industrial Marine	4 3 2	23 13 8	26 16 10	43 30 18	45 26	37	42			

*Based on Figures 1a, 1b and 1c

GALFAN TECHNICAL RESOURCE CENTER

Research Triangle Park, NC, USA

TABLE FIVE

,	TWO-	TWO-SIDE COATING MASS (G/M2) FOR YEARS OF USEFUL LIFE*										
Type Coating		Two-side Coating Mass, g/m2										
and Atmosphere	5	10	15	20	25	30	35	40	45	50		
Regular Galvanize												
Rural	108	185	263	340	418	495	573	650	728	805		
Industrial	177	314	452	589	727	864	1002					
Marine	221	403	584	766	947							
Gallan	62	96	100	122	155	178	201	224	247	270		
Kurai Industrial	100	127	109	190	206	233	250	286	312	330		
Industrial	100	127		100	200	250	205	441	197			
Marine	121	167	212	258	304	330	393	441	487			

TABLE SIX

	TWO-	TWO-SIDE COATING MASS (G/M2) FOR YEARS TO RED RUST*								
Type Coating		Two-side Coating Mass, g/m2								
and Atmosphere	5 10 15 20 25 30 35 44							40	45	50
Regular Galvanize										
Rural	217	297	377	457	537	617	697	777	857	937
Industrial	284	434	584	734	884	1034				
Marine	333	533	733	933	1133	[•			
Galfan						, <u> </u>				
Rural	105	127	150	172	195	217	240	262	285	
Industrial	144	170	195	221	247	273				-
Marine	158	203	249	295]		-			

*Based on Figures 1a, 1b and 1c (extrapolated from Nisshin Steel Co.'s Seven Year Tests)

~

FIGURE 1a

Reg. Galvanize vs. Galfan Corrosion: Rural



(Data extrapolated from Nisshin 7-year study)







(Data extrapolated from Nisshin 7-year study)

FIGURE 1c

Reg. Galvanize vs. Galfan Corrosion: Marine



(Data extrapolated from Nisshin 7-year study)

GALFAN TECHNICAL RESOURCE CENTER

Research Triangle Park, NC, USA

These Tables can be used to accurately and quickly convert one-side GALFAN coating thicknesses to two-side coating weights and vice versa.

		<u> </u>	<u>го ме</u>	TRIC	rwo-s	SIDE V	/EIGH	T		
	TWO-S	SIDE GA	ALFAN	COATI	NG WE	IGHT I	N GRAM	1S/SQ.N	IETER	
		GAL	FAN CO	DATING	THICK	NESS, I	N MICR	ONS		
					UNITS					
TENS	0	1	2	3	4	5	6	7	8	9
0	0	13	26	40	53	66	79	92	106	119
10	132	145	158	172	185	198	211	224	238	251
20	264	277	290	304	317	330	343	356	370	383
30	396	409	422	436	449	462	475	488	502	515
40	528	541	554	568	581	594	607	620	634	647
50	660	673	686	700	713	726	739	752	766	779

CONVERTING ONE-SIDE GALFAN THICKNESS TO METRIC TWO-SIDE WEIGHT

To find the two-side coating weight from a one-side Galfan coating thickness in microns, enter the TENS row, move horizontally to the UNIT column and read the two-side coating weight in grams/sq.meter. To find the approximate one-side Galfan coating thickness, find the nearest two-side coating weight in the chart, read horizontally to the left to find the TENS and then up, adding the UNITS.

Example: The two-side coating weight for 34 microns of one-side thickness is 449 gr/sq.meter. The thickness on each side for a two-side coating weight of 275 gr/sq.meter is approximately 21 microns

]	ΓΟ ΕΝ	GLISH	TWO	SIDE	WEIGI	HT		
	TWC)-SIDE (JALFAN	I COATI	ING WE	IGHT IN	OUNC	ES/SQ.F	TOOT	
		GAL	FAN CO	DATING	THICK	NESS, II	N MICR	ONS		
					UNITS					
TENS	0	1	2	3	4	5	6	7	8	9
0	0.00	0.04	0.09	0.13	0.17	0.22	0.26	0.30	0.34	0.39
10	0.43	0.47	0.52	0.56	0.60	0.65	0.69	0.73	0.77	0.82
20	0.86	0.90	0.95	0.99	1.03	1.08	1.12	1.16	1.20	1.25
30	1.29	1.33	1.38	1.42	1.46	1.51	1.55	1.59	1.63	1.68
40	1.72	1.76	1.81	1.85	1.89	1.94	1.98	2.02	2.06	2.11
50	2.15	2.19	2.24	2.28	2.32	2.37	2.41	2.45	2.49	2.54

CONVERTING ONE-SIDE GALFAN THICKNESS TO ENGLISH TWO-SIDE WEIGHT



GALFAN TECHNICAL RESOURCE CENTER

Research Triangle Park, NC, USA

These Tables can be used to accurately and quickly convert one-side REGULAR GALVANIZING coating thicknesses to two-side coating weight and vice versa

CONVERTING ONE-SIDE REGULAR GALVANIZE THICKNESS TO METRIC TWO-SIDE WEIGHT

TWO-	SIDE RE	EGULAR	GALV	ANIZIN	G COAT	ING WI	EIGHT I	N GRAN	AS/SQ.N	IETER
	REGULAR GALVANIZING COATING THICKNESS, IN MICRONS									
					UNITS					
TENS	0	1	2	3	4	5	6	7	8	9
0	0	14	29	43	57	71	86	100	114	129
10	143	157	171	186	200	214	228	243	257	271
20	286	300	314	328	343	357	371	386	400	414
30	428	443	457	471	486	500	514	528	543	557
40	571	585	600	614	628	643	657	671	685	700
50	714	728	743	757	771	785	800	814	828	843

To find the two-side coating weight from a one-side regular galvanizing coating thickness in microns, enter the TENS row, move horizontally to the UNIT column and read the two-side coating weight in grams/sq.meter. To find the approximate one-side regular galvanizing coating thickness, find the nearest two-side coating weight in the chart, read horizontally to the left to find the TENS and then up, adding the UNITS.

Example: The two-side coating weight for 32 microns of one-side thickness is 457 gr/sq.meter. The thickness on each side for a two-side coating weight of 275 gr/sq.meter is approximately 19.5 microns

CONVERTING ONE-SIDE REGULAR GALVANIZE THICKNESS TO ENGLISH TWO-SIDE WEIGHT

TWO-	SIDE RI	EGULA	R GALV	ANIZIN	G COA	TING W	EIGHT I	N OUN	CES/SQ.	FOOT
REGULAR GALVANIZING COATING THICKNESS, IN MICRONS										
TENS	0	1	2	2		5	6	7	9	
TENS	<u> </u>	L	<u> </u>					·		
0	0.00	0.05	0.09	0.14	0.19	0.23	0.28	0.33	0.37	0.42
10	0.47	0.51	0.56	0.60	0.65	0.70	0.74	0.79	0.84	0.88
20	0.93	0.98	1.02	1.07	1.12	1.16	1.21	1.26	1.30	1.35
30	1.40	1.44	1.49	1.53	1.58	1.63	1.67	1.72	1.77	1.81
40	1.86	1.91	1.95	2.00	2.05	2.09	2.14	2.19	2.23	2.28
50	2.33	2.37	2.42	2.46	2.51	2.56	2.60	2.65	2.70	2.74



W Tree

SECTION III

CORROSION RESISTANCE OF UNPAINTED GALFAN®

ILZRO has historically sponsored research which leads to the *scientific explanation for Galfan's behavior*. It involves itself with the discovery and explanation of the mechanisms behind Galfan's performance in various environments and in the investigation of influences from alloy composition and process variables.

The Galfan Technical Resource Center's (GTRC) task is to *translate* that scientific knowledge into technical information that will promote the manufacturing and use of Galfan throughout the world. The technical information is needed by:

- (1) The licensed alloy producers;
- (2) The licensed Galfan coated steel producers; and
- (3) The regional Galfan development organizations.

ILZRO's research has collected a wealth of valuable scientific knowledge about Galfan but our pursuit of knowledge is a *means to an end* not an end unto itself. Even GTRC's translation of scientific knowledge into technical information has no commercial worth by itself. It also must be a means to an end. One of America's sales gurus said, "Nothing happens until somebody *sells* something." There is an obvious truth contained in that oversimplified hyperbole.

Long-term testing has repeatedly confirmed conclusions drawn from earlier research but that too should be used in every way possible to persuade specifiers, converters, and buyers that Galfan will benefit them in measurable and tangible ways. This has been the strategy used successfully by many new products including Galvalume. Galfan has three major advantages over other zinc or zinc-aluminum coatings in most applications:

- 1. It is more corrosion resistant;
- 2. It is more formable; and
 - 3. It is a better pre-paint coating.

GTRC has set out to present technical information in three booklets (one for each feature) in which we directly and effectively identify the benefits available to the user from these features. The first of the booklets is *Corrosion Resistance of Unpainted Galfan*. The benefit described is the *lower owning cost* for Galfan coated steel as it can be determined in applications such as:

- 1. Corrugated and profiled building panels
- 2. Highway guardrail
- 3. Culverts and corrugated pipe
- 4. Fence systems
- 5. Flat sheet

This paper has been published as a booklet which has a *commercial* objective. Galfan's science and technology is used to support the commercial claims.

The Galfan Panel Cost Study is an example of the simple spreadsheet computer program which has been developed by GTRC to show long-term cost for corrugated or profiled building panels, comparing regular galvanized sheet to Galfan sheet. These programs are available to *active* Licensees on 3.5 inch discs for MS-DOS using Excel.

APPENDIX A

Galfan Panel Cost Studies

English Version

Galfan Panel Cost Studies is a computer program which quickly computes and displays the data which is pertinent when comparing the cost of unpainted Galfan galvanized steel panels to regular galvanized. It is copyrighted by GTRC but permission is hereby given to any Galfan Licensee to copy or use it in any appropriate way to promote the use of Galfan.

GTRC can furnish the Galfan Licensee with the programs (in English and Metric units) on a 3-1/2 inch diskette for use in an IBM compatible computer with MS-DOS. The program is written on Excel For Windows software.

The program is based on data from the paper, *The Improved Corrosion Resistance* of Unpainted Galfan Galvanized Steel by J. L. Hostetler. It requires six inputs from the User which are then used to compute cost analyses and display them for three types of exposure environments; rural, industrial and marine.

User Inputs

<u>Line 1</u> CRS PANEL THICKNESS Enter the gauge thickness of the panel steel sheet in inches.

Line 2PROFILE LOSSESEnter the losses in %. If you do not know the exact losses, pick one from
the Typical Section Table. The profile loss is the ratio of (the difference
between the weight of 100 ft² of installed profiled panel and 100 ft² of
flat CRS) divided by the weight of 100 ft² of CRS.

Line 3 COATING MASS Enter the nominal two-side coating mass in oz/ft². For example, a GF90 grade should be entered as .90.

Line 5	COST OF REGULAR GALVANIZED SHEET
Line 6	COST OF GALFAN GALVANIZED SHEET
	Enter the selling price per short ton for each. The computed cost data displayed in the Output Section will be in the same currency units as this
	input currency.

<u>Line 7</u> <u>LIFE OF THE BUILDING OR YEARS TO AMORTIZE</u> Enter the years of design life for the building or the years the cost analysis is based on.

Displayed Outputs

English Version

Line 8	<u>PANEL WEIGH</u> T
	The program displays the <i>installed profiled</i> panel weight in lbs/ft ² . computed from lines 1 and 2.
Line 9	PANEL YIELD The yield in Ft ² /ton is found by 2,000 lbs/ton divided by line 2.
Line 11	COST PER 100 FT^2 The cost for 100 Ft^2 of each type galvanized panel is shown. It is computed from line 5 (or 6) divided by line 9 times 100 (ft^2).
<u>Line 13</u>	YEARS OF USEFUL LIFE The program computes the years of exposure required to corrode the total coating thickness based on data from Nisshin Steel's tests and the extrapolations shown in Figures 1a, b and c.
Line 15	COST PER YEAR/100 FT ²
<u>Line 16</u>	Line 12 divided by line 14.
<u>Line 17</u>	SAVINGS WITH GALFAN PER 100 FT ² Per year = line 15 - line 16 For the life of the building = line 17 times line 7.
<u>Line 19</u>	YEARS TO RED RUST The preceding data uses the <i>total years of useful life</i> before replacing the panel. This last Section assumes the panels will be replaced when red rust appears. The program computes the years of exposure to corrode the coating to a thickness where red rust will appear. It uses 0.37 oz/ft ² for regular galvanized and 0.17 oz/ft ² for Galfan galvanized.
<u>Line 21</u>	<u>COST PER YEAR/100 FT²</u> Line 11 (or 12) divided by line 18 (or 19).
<u>Line 23</u>	SAVINGS WITH GALFAN
<u>Line 24</u>	For the life of the building = line 23 times line 7.

GALFAN PANEL COST STUDIES (Eng)

GALFAN PANEL CO

GALFAN LICENSEE:			
CUSTOMER:			
DATE	FILENAME:	Panel 1	
	INDUTO		

		-	
1	CRS panel thickness, inches	0.012	NOTES
2	Profile loss, %	20	
3	Coating mass, ounces/sq.foot	0.90	1.
		275	
5	Cost of regular galvanize sheet	600	1
6	Cost of Galfan sheet	625	
7	Life of building or years to ammortize	50	

DISPLAY OUTPUTS

	A	TMOSPHER	E
	RURAL	INDUSTRIAL	MARINE
8 Panel weight, Lbs/Sq.ft.	0.60	0.60	0.60
9 Panel yield, sq.ft/ton	3321	3321	3321
10 Galvanize alloy used, Lbs./100 sq.feet	6.8	6.8	6.8
11 Cost per 100 sq.feet: Regular Galvanize	18.07	18.07	18.07
12 Galfan	18.82	18.82	18.82
13 Years of useful life: Regular Galvanize	15.5	8.4	6.4
14 Galfan	51.0	37.7	21.9
15 Cost per year/100 sq.ft. Regular Galvanize	1.17	2.16	2.83
16 Galfan	0.37	0.50	0.86
17 Savings with GALFAN per year	0.80	1.66	1.97
18 per 100 sq.ft.: Life of building	39.93	83.10	98.50
19 Years to red rust: Reg Galvanize	8.0	4.5	3.4
20 Galfan	39.6	27.7	16.f
21 Cost per year/100 sq.ft.: Regular Galvanize	2.25	4.06	5.29
22 Galfan	0.46	0.65	1.12
23 Savings with GALFAN per year	1.79	3.40	4.17
24 per 100 sq.ft.: Life of building	88.79	168.85	205.97

GALFAN TECHNICAL RESOURCE CENTER

Research Triangle Park, NC, USA

GALFAN LICENSEE:	
CUSTOMER:	
DATE	

INPU

1 CRS panel thickness, inches

2 Profile loss, %

3 Coating mass, ounces/sq.foot

5 Cost of regular galvanize sheet

6 Cost of Galfan sheet

7 Life of building or years to ammortize

DISPLAY

8	Panel weight, Lbs/Sq.ft.
9	Panel vield, so ft/ton

9 Panel yield, sq.ft/ton
10 Galvanize alloy used, Lbs./100 sq.feet

11 Cost per 100 sq.feet: Regular Galvaniz Galfa 12 Regular Galvaniz 13 Years of useful life: Galfa Regular Galvaniz 15 Cost per year/100 sq.ft. Galfa 16 17 Savings with GALFAN per yea Life of buildir 18 per 100 sq.ft.:

 19 Years to red rust:
 Reg Galvania

 20
 Galfa

 21 Cost per year/100 sq.ft.:
 Regular Galvania

 22
 Galfa

 23 Savings with GALFAN
 per yea

 24
 per 100 sq.ft.:
 Life of buildir

GALFAN PANEL COST STUDIES (Eng)

GALFAN PANEL C

CUSTOMER:	
10.175	 FILENAME:

10

INPUT	S		
1 CBS panel thickness, inches	0.036	NOTES	
2 Profile loss. %	20		
3 Coating mass, ounces/sq.foot	0.90		
o oodang meter, tensoroquet	275		
5 Cost of regular galvanize sheet	600		1
6 Cost of Galfan sheet	625		
7 Life of building or years to ammortize	50		

Panel 3

DISPL	AY O	UTP	UTS
		-	

	4	TMOSPHER	Ε
	RURAL	INDUSTRIAL	MARINE
8 Panel weight, I bs/Sq.ft.	1.81	1.81	1.81
9 Panel vield so ft/ton	1107	1107	1107
10 Gaivanize alloy used, Lbs./100 sq.feet	6.8	6.8	6.8
11 Cost per 100 sq.feet: Regular Galvanize	54.20	54.20	54.20
12 Galfan	56.46	56.46	56.46
13 Years of useful life: Regular Galvanize	15.5	8.4	6.4
14 Galfan	51.0	37.7	21.9
15 Cost per year/100 sq.ft. Regular Galvanize	3.50	6.48	8.49
16 Galfan	1.11	1.50	2.58
17 Savings with GALFAN per year	2.40	4.99	5.91
18 per 100 sq.ft.: Life of building	119.79	249.30	295.51
19 Years to red rust: Reg Galvanize	8.0	4.5	3.4
20 Galfan	39.6	27.7	<u> </u>
21 Cost per year/100 sq.ft.: Regular Galvanize	6.75	12.17	15.86
22 Galfan	1.37	1.95	3.36
23 Savings with GALFAN per year	5.38	10.21	12.50
24 per 100 sq.ft.: Life of building	266.36	506.55	617.91

GALFAN TECHNICAL RESOURCE CENTER Research Triangle Park, NC, USA

CUSTOMER: DATE INPL

- 1 CRS panel thickness, inches
- 2 Profile loss, %

GALFAN LICENSEE:

- 3 Coating mass, ounces/sq.foot
- 5 Cost of regular galvanize sheet
- 6 Cost of Galfan sheet
- 7 Life of building or years to ammortize

DISPLA

8	Panel weight, Lbs/Sq.ft.	
9	Panel yield, sq.ft/ton	
10	Galvanize alloy used, Lbs	s./100 sq.feet
11	Cost per 100 sq.feet:	Regular Galvan
12		Gal
13	Years of useful life:	Regular Galvan
14		Gal
15	Cost per year/100 sq.ft.	Regular Galvan
16		Gal
17	Savings with GALFAN	per y
18	per 100 sq.ft.:	Life of build
19	Years to red rust:	Reg Galvar
20		Gai
21	Cost per year/100 sq.ft.:	Regular Galvar
22		Gal
23	Savings with GALFAN	per y
24	per 100 sq.ft.:	Life of build

III-6

GALFAN PANEL COST STUDIES (Eng)

GALFAN PANEL CO

GALFAN LICENSEE:			
CUSTOMER:			
DATE	FILENAME:	Panel 5	

	INPUTS				
1	CRS panel thickness, inches	0.024	NOTES		
2	Profile loss, %	20			
3	Coating mass, ounces/sg.foot	0.60			
Ŭ		183			
5	Cost of regular galvanize sheet	600			
6	Cost of Galfan sheet	625			
7	Life of building or years to ammortize	50	_1		
· · · ·					

DISPLAY OUTPUTS

		In the local division of the local divisiono	
	A	TMOSPHER	E
	RURAL	INDUSTRIAL	MARINE
8 Panel weight, Lbs/Sg.ft.	1.20	1.20	1.20
9 Panel vield, so ft/ton	1661	1661	1661
10 Galvanize alloy used, Lbs./100 sq.feet	4.5	4.5	4.5
11 Cost per 100 so.feet: Regular Galvanize	36.13	36.13	36.13
12 Galfan	37.64	37.64	37.64
13 Years of useful life: Regular Galvanize	9.4	5.2	4.0
14 Galfan	31.2	20.4	11.9
15 Cost per year/100 sq.ft. Regular Galvanize	3.83	6.94	9.06
16 Galfan	1.21	1.84	3.15
17 Savings with GALFAN per year	2.62	5.10	5.91
18 per 100 sq.ft.: Life of building	131.14	255.02	295.65
19 Years to red rust: Reg Galvanize	2.9	1.7	1.3
20 Galfan	19.8	10.4	6.2
21 Cost per year/100 sq.ft.: Regular Galvanize	12.64	21.83	28.21
22 Galfan	1.83	3.47	5.80
23 Savings with GALFAN per year	10.81	18.36	22.41
24 per 100 sq.ft.: Life of building	536.84	910.66	1108.65

GALFAN TECHNICAL RESOURCE CENTER

Research Triangle Park, NC, USA

GALFAN LICENSEE: CUSTOMER: DATE

INPU

- 1 CRS panel thickness, inches
- 2 Profile loss, %
- 3 Coating mass, ounces/sq.foot
- 5 Cost of regular galvanize sheet 6 Cost of Galfan sheet
- 7 Life of building or years to ammortize

DISPLAY

8	Panel weight, Lbs/Sq.ft.	
9	Panel yield, sq.ft/ton	
10	Galvanize alloy used, Lbs	./100 sq.feet
11	Cost per 100 sq.feet:	Regular Galvaniz
12		Galfa
13	Years of useful life:	Regular Galvaniz
14		Galfa
15	Cost per year/100 sq.ft.	Regular Galvaniz
16		Galfa
17	Savings with GALFAN	per yea
18	per 100 sq.ft.:	Life of buildin
19	Years to red rust:	Reg Galvaniz
20	I	Galfa
21	Cost per year/100 sq.ft.:	Regular Galvaniz
22		Galfa
23	Savings with GALFAN	per yea
24	per 100 sq.ft.:	Life of buildin

Additional Savings

English Version

The savings shown are based on 100 ft^2 of installed profiled panel. The *total* savings for a complete building using the panels is found by dividing the total installed area by 100 and multiplying that by the savings shown. For example:

Assume a 50 year life for a building in an industrial environment with $8,000 \text{ ft}^2$ of corrugated roofing panels having a 20% profile loss. Find the total Galfan savings if the panels are .024 gauge with .90 oz/ft² coating.

(1) Divide 8,000 by 100 = 80

(2) From the Galfan Panel Cost Studies, find the 50 year savings to be $$166.20 \text{ per } 100 \text{ ft}^2$.

(3) Multiply \$166.20 by 80 = \$13,296, the total Galfan panel savings for the building in 50 years.

The Galfan savings shown here are only the savings on the purchase of the original and replacement panels. There are additional savings from:

... Escalation in prices over the amortized period

... Transporting and handling the replacement panels

... Disposal of the replaced panels

... Labor to remove the replaced panels

... Labor to install the replacement panels

... Allowance for damage to adjacent materials

... Cost of new fasteners and attachments

Considering these other costs, the *total overall cost to own* the roof may easily be 2 to 5 times the savings shown for the panels only.

APPENDIX A

Galfan Panel Cost Studies

Metric Version

Galfan Panel Cost Studies is a computer program which quickly computes and displays the data which is pertinent when comparing the cost of unpainted Galfan galvanized steel panels to regular galvanized. It is copyrighted by GTRC but permission is hereby given to any Galfan Licensee to copy or use it in any appropriate way to promote the use of Galfan.

GTRC can furnish the Galfan Licensee with the programs (in English and Metric units) on a 3-1/2 inch diskette for use in an IBM compatible computer with MS-DOS. The program is written on Excel For Windows software.

The program is based on data from the paper, *The Improved Corrosion Resistance* of Unpainted Galfan Galvanized Steel by J. L. Hostetler. It requires six inputs from the User which are then used to compute cost analyses and display them for three types of exposure environments; rural, industrial and marine.

User Inputs

Line 1 CRS PANEL THICKNESS

Enter the gauge thickness of the panel steel sheet in mm.

- <u>Line 2</u> <u>PROFILE LOSSES</u> Enter the losses in %. If you do not know the exact losses, pick one from the Typical Section Table. The profile loss is the ratio of (the *difference* between the weight of 100 m² of *installed profiled* panel and 100 m² of flat CRS) divided by the weight of 100 m² of CRS.
- <u>Line 3</u> COATING MASS Enter the nominal two-side coating mass in g/m².
- Line 5 COST OF REGULAR GALVANIZED SHEET

COST OF GALFAN GALVANIZED SHEET Enter the selling price per short ton for each. The computed cost data displayed in the Output Section will be in the same currency units as this input currency.

<u>Line 7</u> LIFE OF THE BUILDING OR YEARS TO AMORTIZE Enter the years of design life for the building or the years the cost analysis is based on.

Line 6

Displayed Outputs

Metric Version

<u>Line 8</u>	<u>PANEL WEIGHT</u>
	The program displays the installed profiled panel weight in kg/m ² .
	computed from lines 1 and 2.
Line 9	PANEL YIELD
	The yield in m^2 /tonne is found by 1,000 kg/tonne divided by line 2.
<u>Line 11</u>	COST PER 100 m ²
	The cost for 100 m ² of each type galvanized panel is shown. It is computed from line 5 (or 6) divided by line 9 times 100 (m ²).
<u>Line 13</u>	YEARS OF USEFUL LIFE
	The program computes the years of exposure required to corrode the total coating thickness based on data from Nisshin Steel's tests and the extrapolations shown in Figures 1a, b and c.
<u>Line 15</u>	COST PER YEAR/100 m ²
T · 16	Line 11 divided by line 13.
Line 16	Line 12 divided by line 14.
<u>Line 17</u>	SAVINGS WITH GALFAN PER 100 m ²
	Per year = line 15 - line 16
	For the life of the building = line 17 times line 7.
Line 19	YEARS TO RED RUST
	The preceding data uses the total years of useful life before replacing the
	panel. This last Section assumes the panels will be replaced when red rust
	coating to a thickness where red rust will appear. It uses 114 g/m^2 for
	regular galvanized and 53 g/m ² for Galfan galvanized.
Line 21	COST PER YEAR/100 m ²
	Line 11 (or 12) divided by line 18 (or 19).
Line 23	SAVINGS WITH GALFAN
	Per year = line 21 - line 22
<u>Line 24</u>	For the life of the building = line 23 times line 7.

GALFAN PANEL COST STUDIES (Met)

FILENAME:

PANEL 1

GALFAN LICENSEE:
CUSTOMER:
DATE

	INPUTS				
1	CRS panel thickness, mm	0.20	NOTES		
2	Profile loss, %	20			
3	Coating mass, grams/sq.meter	275			
ł		275			
5	Cost of regular galvanize sheet	660			
6	Cost of Galfan sheet	688			
17	Life of building or years to ammortize	50	<u> </u>		

DISPLAY OUTPUTS

A	TMOSPHER	E
RURAL	INDUSTRIAL	MARINE
1.93	1.93	1.93
518	518	518
33.0	33.0	33.0
127.32	127.32	127.32
132.72	132.72	132.72
15.5	8.4	6.4
51.1	37.8	21.9
8.21	15.20	19.91
2.60	3.51	6.06
5.61	11.69	13.85
280.67	584.35	692.62
8.1	4.5	3.4
39.7	27.8	16.2
15.81	28.48	37.12
3.21	4.57	7.86
12.60	23.90	29.25
623.04	1185.42	1445.93
	A RURAL 1.93 518 33.0 127.32 132.72 15.5 51.1 8.21 2.60 5.61 280.67 8.1 39.7 15.81 3.21 12.60 623.04	ATMOSPHER RURAL INDUSTRIAL 1.93 1.93 518 518 33.0 33.0 127.32 127.32 132.72 132.72 15.5 8.4 51.1 37.8 8.21 15.20 2.60 3.51 5.61 11.69 280.67 584.35 8.1 4.5 39.7 27.8 15.81 28.48 3.21 4.57 12.60 23.90 623.04 1185.42

GALFAN TECHNICAL RESOURCE CENTER

Research Triangle Park, NC, USA

GALFAN PANEL C

GALFAN LIC	ENSEE:
CUSTOMER:	

DATE

INPL

- 1 CRS panel thickness, mm
- 2 Profile loss, %
- 3 Coating mass, grams/sq.meter
- 5 Cost of regular galvanize sheet
- 6 Cost of Galfan sheet
- 7 Life of building or years to ammortize

DISPLAY

8	Panel weight, Kg/sq.m			
9	Panel yield, sq.meter/tonne			
10	Galvanize alloy used, Kg	/100 sq.meter		
11	Cost per 100 sq.meter:	Regular Galvan		
12		Gall		
13	Years of useful life:	Regular Galvan		
14		Gall		
15	Cost per year/100 sq.m	Regular Galvan		
16		Gali		
17	Savings with GALFAN	per ye		
18	per 100 sq.m:	Life of buildi		
19	Years to red rust:	Reg Galvani		
20		Gall		
21	Cost per year/100 sq.m.:	Regular Galvani		
22		Galf		
23	Savings with GALFAN	per ye		
24	per 100 sq.m.:	Life of buildi		

GALFAN PANEL COST STUDIES (Met)

GALFAN PANEL CC

GALFAN LICENSEE:		
CUSTOMER:		
DATE	FILENAME:	PANEL 3

INPUTS

1 CRS panel thickness, mm	0.60 NOTES
2 Profile loss, %	20
3 Coating mass, grams/sq.meter	275
	275
5 Cost of regular galvanize sheet	660
6 Cost of Galfan sheet	688
7 Life of building or years to ammortize	50

DISPLAY OUTPUTS

	ATMOSPHERE		
	RURAL	INDUSTRIAL	MARINE
8 Panel weight, Kg/sq.m	5.79	5.79	5.79
9 Panel vield, sg.meter/tonne	173	173	173
10 Galvanize alloy used, Kg./100 sq.meter	33.0	33.0	33.0
11 Cost per 100 sq.meter: Regular Galvanize	381.97	381.97	381.97
12 Galfan	398.17	398.17	398.17
13 Years of useful life: Regular Galvanize	15.5	8.4	6.4
14 Galfan	51.1	37.8	21.9
15 Cost per year/100 sq.m Regular Galvanize	24.63	45.59	59.73
16 Galfan	7.79	10.52	18.18
17 Savings with GALFAN per year	16.84	35.06	41.56
18 per 100 sq.m: Life of building	842.01	1753.04	2077.85
19 Years to red rust: Reg Galvanize	8.1	4.5	3.4
20 Galfan	39.7	27.8	16.2
21 Cost per year/100 sq.m.: Regular Galvanize	47.42	85.43	111.35
22 Galfan	9.63	13.72	23.59
23 Savings with GALFAN per year	37.79	71.71	87.76
24 per 100 sq.m.: Life of building	1869.12	3556.27	4337.78

GALFAN LICENSEE: CUSTOMER:

DATE

INPUT

1 CRS panel thickness, mm

2 Profile loss, %

3 Coating mass, grams/sq.meter

5 Cost of regular galvanize sheet

6 Cost of Galfan sheet

7 Life of building or years to ammortize

DISPLAY

8	Panel weight, Kg/sq.m	
9	Panel yield, sq.meter/tonr	9
10	Galvanize alloy used, Kg.	/100 sq.meter
11	Cost per 100 sq.meter:	Regular Galvanize
12		Galfar
13	Years of useful life:	Regular Galvanize
14		Galfar
15	Cost per year/100 sq.m	Regular Galvanize
16		Galfa
17	Savings with GALFAN	рег уеа
18	per 100 sq.m:	Life of building
19	Years to red rust:	Reg Galvaniz
		Galfa
21	Cost per year/100 sq.m.:	Regular Galvaniz
22		Galfa
23	Savings with GALFAN	per yea
24	per 100 sq.m.	: Life of buildin

GALFAN TECHNICAL RESOURCE CENTER Research Triangle Park, NC, USA

GALFAN PANEL COST STUDIES (Met)

GALFAN LICENSEE:		
CUSTOMER:	-	
DATE	FILENAME:	PANEL 5

INPUTS				
1	CRS panel thickness, mm	0.40	NOTES	
2	Profile loss, %	20		
3	Coating mass, grams/sq.meter	185		
		185		·• .
5	Cost of regular galvanize sheet	660		
6	Cost of Galfan sheet	688		
7	Life of building or years to ammortize	50		

DISPLAY OUTPUTS

	ATMOSPHERE		
	RURAL	INDUSTRIAL	MARINE
8 Panel weight, Kg/sq.m.,	3.86	3.86	3.86
9 Panel yield, sq.meter/tonne	259	259	259
10 Galvanize alloy used, Kg./100 sq.meter	22.2	22.2	22.2
11 Cost per 100 sq.meter: Regular Galvanize	254.64	254.64	254.64
12 Galfan	265.45	265.45	265.45
13 Years of useful life: Regular Galvanize	9.6	5.3	4.0
14 Galfan	31.6	20.8	12:2
15 Cost per year/100 sq.m Regular Galvanize	26.64	48.32	63.07
16 Galfan	8.40	12.77	21.82
17 Savings with GALFAN per year	18.24	35.55	41.25
18 per 100 sq.m: Life of building	911.96	1777.72	2062.55
19 Years to red rust: Reg Galvanize	3.0	1.7	1.3
20 Galfan	20.2	10.8	6.5
21 Cost per year/100 sq.m.: Regular Galvanize	86.03	148.76	192.31
22 Galfan	12.61	23.60	39.48
23 Savings with GALFAN per year	73.42	125.16	152.83
24 per 100 sq.m.: Lile of building	3644.19	6207.94	7557.92

GALFAN TECHNICAL RESOURCE CENTER Research Triangle Park, NC, USA

GALFAN PANEL CC

GALFAN LICENSEE:	
CUSTOMER:	

DATE

INPUT

- 1 CRS panel thickness, mm
- 2 Profile loss, %
- 3 Coating mass, grams/sq.meter
- 5 Cost of regular galvanize sheet 6 Cost of Galfan sheet
- 7
- Life of building or years to ammortize

DISPLAY (

8	Panel weight, Kg/sq.m		
9	Panel yield, sq.meter/tonne		
10	Galvanize alloy used, Kg.	/100 sq.meter	
11	Cost per 100 sq.meter:	Regular Galvanize	
12		Galfar	
13	Years of useful life:	Regular Galvanize	
14		Galfar	
15	Cost per year/100 sq.m	Regular Galvanize	
16		Galfar	
17	Savings with GALFAN	per yea	
18	per 100 sq.m:	Life of building	
19	Years to red rust:	Reg Galvanize	
20		Galfar	
21	Cost per year/100 sq.m.:	Regular Galvanize	
22		Galfar	
23	Savings with GALFAN	per yea	
24	per 100 sq.m.:	Life of building	

Additional Savings

Metric Version

The savings shown are based on 100 m^2 of installed profiled panel. The *total* savings for a complete building using the panels is found by dividing the total installed area by 100 and multiplying that by the savings shown. For example:

Assume a 50 year life for a building in an industrial environment with 750 m² of corrugated roofing panels having a 20% profile loss. Find the total Galfan savings if the panels are 0.6 gauge with 275 g/m² coating.

(1) Divide 750 by 100 = 7.5

(2) From the Galfan Panel Cost Studies, find the 50 year savings to be $1753.04 \text{ per } 100 \text{ m}^2$.

(3) Multiply 1753.04 by 7.5 = 13,147, the total Galfan panel savings for the building in 50 years.

The Galfan savings shown here are only the savings on the purchase of the original and replacement panels. There are additional savings from:

... Escalation in prices over the amortized period

... Transporting and handling the replacement panels

... Disposal of the replaced panels

... Labor to remove the replaced panels

... Labor to install the replacement panels

... Allowance for damage to adjacent materials

... Cost of new fasteners and attachments

Considering these other costs, the *total overall cost to own* the roof may easily be 2 to 5 times the savings shown for the panels only.
III-14

SECTION III APPENDIX

QUESTIONS AND ANSWERS

Williams: My question has to do with the alloy layer (or absence thereof) in a GALFAN coating and its contribution to corrosion resistance. I think you mentioned its thickness was 1 micron or less. How is it controlled?

Hostetler: Typically, on a sheet product, you would not even see a "layer" as such. If we had a good micrograph here, you might see a dark line which indicates there is an intermetallic transition at the interface which is different from the steel and the coating.

The mention of GALFAN's intermetallic layer being more effective against corrosion and appearance of red rust was taken from Bekaert's study on GALFAN wire which was made by the double dip process in which the classic binary Fe-Zn alloy layer is formed in the first dip (zinc) but is transformed into a ternary Al-Fe-Zn intermetallic which is relatively ductile, passive and cathodic when it is dipped in the GALFAN bath.

<u>Williams:</u> Is the angle made by the product's installation important in its rate of corrosion?

Hostetler: I will let others in the room respond to that but I am sure there is a difference depending upon whether the product is rain-washed, in direct sunlight or in the shade, and upon many other variables. I noticed, however, in studying the long-term exposure tests by CRM, Bekaert, New Zealand Steel and Nisshin that there was reasonably good correlation even though the panels were in different latitudes and probably at different angles, etc.

<u>Dewitte:</u> I want to call everybody's attention to the difficulty in extrapolating results from specific test sites to other locations. I am not afraid of marine or industrial applications but I am afraid when extrapolating rural or semiindustrial to promise years of life that one can never be sure that conditions have been similar.

Dubois:	I wonder whether we should prepare such a book to include edge creep and corrosion at bends (for pre-paint). We probably do not have enough data yet but people want to hear about a typical installation which includes bends and cut edges. This book is a good start in order to show how GALFAN can improve corrosion in plain panels but we should include edges and bends.
Hostetler:	When we get to the third book in this series which will be on pre-painted GALFAN, that information will surely be included.
Nunninghoff:	We tested straight wire and wire with coil diameter = 1 wire diameter. Both performed similarly.
<u>Dubois:</u>	I agree. My point though is that books such as these will be used to promote GALFAN to our customers. It will show them if they are comparing (and I think we should show <i>thickness</i> not g/m^2 because the price will not be the same if we compare equal weight). We should be able to say, "If you take 20 microns GALFAN, regarding the edges, you should not see red rust for (15) years under (these) type of conditions. This is the type of information we should prepare in the future in order to help architects, builders, etc.
Hostetler:	This is the objective that has motivated us to do what we have done so far. I would solicit support from Andy Celestin because he has been using the spread sheets as he discusses GALFAN for use on real applications.
<u>Celestin:</u>	We have used this with architects although this is for bare GALFAN whereas most of the time we are talking about a prepainted product.
	You may remember when Galvalume producers announced their first 20- year guarantee. It may be of interest to know that at the time they did this, they had seven years of outdoor exposure. We already have more than that and it looks very good so I have no problem presenting this kind of information to an architect or anyone else.

This paper was originally presented at the 15th Licensee Meeting in Liege, Belgium. It is shown again in this publication because of its role in the book shown as Section III and because the reproductions of the photos on pages IV-6 and IV-9 in the previous publication were not of good quality.

June 5, 1990

Yusuke Hirose

NISSHIN STEEL CO., LTD.

SECTION IV

1. Introduction

Nisshin Steel Co., Ltd. is producing Zn-5%Al hot-dip coated steel sheets with a brand "Galtite". At first, we presumed the corrosion resistance of "Galtite" based on outdoor exposure test results of both Zn-Al alloy coated steel sheets by Bethlehem Steel, USA and hot-dip galvanized steel sheets by Nisshin Steel (brand "Pentite B") (Fig. 1, Fig. 2, and Fig. 3). However, the result of 7-year outdoor exposure test revealed that "Galtite" is less corroded than "Pentite B" and that it has longer service life (higher corrosion resistance) than expected. Below.is discussed the obtained results.

2. Results

(1) Cross sectional microscopic observation of coated layer of the sample exposed to atmosphere for 7 years revealed that the corrosion depth of "Pentite B" increases linearly with the lapse of exposure time, whereas the corrosion rate of "Galtite" decreases parabolically with the lapse of exposure time. Accordingly, in the first or second year of exposure, there is no significant difference in corrosion depth between them, but as the exposure time elapses (for example, 5 years, 7 years), the difference in corrosion depth between "Galtite" and "Pentite B" becomes more remarkable (Fig. 4,5)

- (2) We calculated the time to red rusting based on the average corrosion rate of coatings for these 7 years and plotted the obtained data on the initially presumed service life curve (Fig. 3) so as to compare them. As a result, it was found that "Galtite" has longer service life than expected in any environment (Fig. 6). Especially, exposure data in industrial environment show that the time to red rusting calculated from the corrosion depth of "Pentite B" and "Galtite" both subjected to 7-year exposure is by far longer than presumed service life. We consider that this is due to the fact that environmental corrosiveness of exposure testing site has become milder than that before.
- (3) The difference in corrosion behavior between "Galtite" and "Pentite B" is assumed to be caused by the difference of corrosion products. The corrosion products on "Pentite B" was found to be composed of both zinc carbonate hydroxide and zinc oxide, irrespective of exposure environments (Fig. 7~10) But in the corrosion products on "Galtite" which were exposed

IV-3

in the three different environments except in severe marine, only the zinc carbonate hydroxide and no zinc oxide was detected. This means that the zinc carbonate hydroxide is formed more stably and easily in "Galtite" than in "Pentite B". In addition, the corrosion products (supposed to be aluminum sulfate hydroxide) consisting of Al-S-O was also detected on "Galtite" (Fig. 11). It is considered that the corrosion of "Galtite" is suppressed as the coated layer is covered by these hydroxides.

- (4) From the results of 7-year exposure testings, we got the corrosion resistance ratio of "Galtite" to "Pentite B" in various environments as follows:
 - . Rural environment 2.04 times
 - . Industrial environment 2.07 times
 - . Severe marine environment 2.16 times



- Fig. 1 Effect of coating weight on corrosion performance of hot-dip galvanized steel sheet("Pentite B").
 - Data by ASTM, A-5 Committe Data by Nisshin Steel



Fig. 3 Life estimation to corrosion of "Galtite" (5%Al-Zn) in various environments.



- Fig. 2 Effect of Al content on corrosion performance of Al-Zn alloy coatings after 5 years' exposure.
 - + J.B.Horton:Corrosion control by Coatings,Science Press, (1987),59





	Thickness	Composi	Coating		
Test panel	(mm)	AI .	Pb	Mg	weight (g/m²)
"Pentile B"	0.35	0. 23	0.17	tr.	160
"Galtite"	0. 35	4.4	0.003	Small amount	156



Fig.5 Cross-sectional microstructures of "Galtite"(5%AI-Zn) and "Pentite B"(Galvanized) sheets exposed for 7 years in various environments.





:life	calcula	ated	from	7	years	exposure	results
-------	---------	------	------	---	-------	----------	---------



Fig.7 Corrosion products formed on "Galtite" and "Pentite B" sheets in rural environment.



Fig. 8 Corrosion products formed on "Galtite" and "Pentite B" sheets in industrial environment.





Fig. 9 Corrosion products formed on "Galtite" and "Pentite B" sheets in marine environment.



Fig.10 Corrosion products formed on "Galtite" and "Pentite B" in severe marine.



a) "Pentite B"(Galvanized)

b) "Galtite" (5 % Al-Zn)

Fig.11 X-ray images of corrosion products formed on "Galtite" and "Pentite B" sheets exposed for 5 years in industrial environment.

IV-10

CORROSION RESISTANCE OF PAINTED ZN-5%A1 COATED STEEL SHEET EXPOSED

OUTDOORS FOR NINE YEARS

<u>Yasuji Kobayashi</u> , Yasuhei Sakamoto , Tenji Ban and Shoji Shijima Kawatetsu Galvanizing Co.,Ltd Chiba, Japan

1. INTRODUCTION

Prepainted Zn-5% Al-O. 1% misch metal steel sheet (GF), as is generally known, exhibits excellent corrosion resistance in outdoor exposure tests while it is inferior to prepainted galvanized (GI) in the salt spray test; specifically, prepainted GF offers less resistance to edge creep in salt spray tests.

In spite of many reports about the corrosion performance of GF, a systematic comparison of the edge creep characteristics during long term outdoor exposure with those of GI and galvannealed (GA), including the effect of pretreatment and the metal coating thickness of GF, has not yet been made.

In the present report, the edge creep width of prepainted GF, GI and GA was examined by outdoor exposure for 9 years and by salt spraying (ASTM B-1 17) for up to 1000 hours. The effect of the type of metal coating, metal coating weight, and pretreatment on edge creep width is described and, based on an analysis of corrosion products, differences in the two test methods are discussed.

2. EXPERIMENTAL METHOD

The steel sheet thickness and metal coating weight of the substrate for painting are given in Table 1. The metal coated surface was pretreated with roll-on type chromate NRC-300 and with zinc phosphate ZD-9000. All sheets

were painted with epoxy primer $(5 \ \mu \text{ m})$ and with an oil-free polyester top coat $(12 \ \mu \text{ m})$. The primer is a conventional type, and does not contain an increased amount of strontium chromate. After painting, the sheets were cut into 200×100 mm pieces for accelerated (salt spray test) and outdoor exposure testing for 9 years at two sites, Choshi(severe marine district) and Chiba(industrial district).

3. RESULTS

3-1. Effect of Substrate and Pretreatment

Figure 1 and Photo 1 show the effect of the substrates and pretreatment method. In the severe marine district, the edge creep width of prepainted GF-B,GI, and GA were 3 and 2 mm,8 and 5 mm, and 15 and 16 mm, for chromated and zinc phosphated respectively. The exposure test of prepainted GA was discontinued after 5.5 years, because the rate of edge creep growth was extremely high. The edge creep widths on zinc phosphated GF and GI were smaller than those on chromated GF-B and GI. This phenomenon was more distinct in the prepainted GI.

In the industrial district, prepainted GF-B and GI showed nearly the same edge creep width, while the width on GA was about two times larger than on GF-B and GI. GF-B with zinc phosphate pretreatment showed a smaller edge creep width, as in the severe marine district exposure.

3-2. Effect of Zinc Metal Coating Weight

Fig. 2 shows the effect of the zinc coating weight of GF on edge creep growth. The edge creep width decreases as the zinc coating weight increases.

ZnO was observed on GI (Fig.6-a), while ZnO and $Zn_6Al_2(OH)_{16}$ CO₃ $4H_2O$ were found on GF(Fig.6-b). The latter corrosion product seems to account for the better corrosion resistance of GF.

4. CONCLUSIONS

An investigation of the effects of the substrate, pretreatment method and zinc coating weight on edge creep in SST and outdoor exposure test was made, with the following conclusions.

- Prepainted GF exhibited excellent corrosion in severe marine exposure for 9 years, in comparison with prepainted GI and GA.
- 2) The edge creep width on zinc phosphate pretreated specimens was smaller than on roll-on type chromated specimens. This was attributed to the use of conventional type primer in the present experiment.
- With GF, the edge creep width decreases as the zinc coating weight increases.
- 4) The edge creep on GI grows linearly with time both in the SST and outdoor exposure test. Because this relationship dose not exist with GF and GA, it can be concluded that SST is not suitable for estimating the anticorrosivity of prepainted GF and GA.
- 5) Corrosion products which contained aluminum hydroxide were detected on on prepainted GF after severe marine exposure. It was considered that the corrosion of prepainted GF is inhibited by this hydroxide.

<u>Table-1</u>

	GF-A	GF-B	GF-D	GI	GA
Base Thickness(mm)	0.6	0.6	0.6	0.35	0.7
coating Mass (g/m²) F/B	69/71	144/105	195/208	132/128	56/0
Destastast	Roll-on type Chromate 50mgCr/m²				
Pretreatment		Zinc Phos	phate 1.()g/m²	
Primer		Ероху	5.	μm	
Тор		Dil-free	Polyester	12 µ m	

Materials used for painting

<u>Table-2</u>

X-ray Diffraction Analysis of Corrosion Products

	Specimen	Corrosion Products
CCT	Prepainted GI	ZnC1 ₂ •4Zn (OH) 2, 4ZnO•CO ₂ •4H ₂ O
221	Prepainted GF	ZnC1 ₂ •4Zn (OH) 2, 4ZnO•CO ₂ •4H ₂ O
Russes	Prepainted GI	ZnO
Exposure	Prepainted GP	ZnO , ZnsAl2(OH)1sCOs+4H2O.

-

-



Fig.1 Effect of substrate and pretreatment in outdoor exposure test for 9 years (GA exposed 5.5 years)



Roll-on type chromate pretreated Zinc phosphate pretreated



Photo.1 Edge creep width after severe marine exposure for 9 years (GA exposed 5.5 years)



Fig. 2 Effect of zinc coating weight on edge creep width in outdoor exposure test for 9 years













Fig. 4 Edge creep width by SST and severe marine exposure (Zinc phosphate pretreted)



Fig. 5 X-ray diffraction of SST corrosion product (prepainted GI and GF)



Fig. 6 X-ray diffraction of corrosion product in severe marine district exposure test

QUESTIONS AND ANSWERS

Gerenrot:	Do you make the conclusion that chromating and phosphating give the same results for pre-treatment?
Kobayashi:	Yes. They are generally comparable.
Leroy:	I would like to ask about your phosphating solution. Do you have any fluoride additions?
Kobayashi:	No. It is a zinc phosphate with no fluorides.
Dewitte:	This shows there is no correlation between the salt spray test (SST) and outdoor exposure when comparing GALFAN with GI and GA. Can you explain why this is so?
<u>Kobayashi:</u>	It seems when regular galvanized and GALFAN are exposed to SST, the same corrosion products are left. When subjected to outdoor exposure, however, we see that ZnO is the corrosion product left on GI but on GF they include zinc-aluminum hydroxides and carbonates.
<u>Chairman:</u>	I am reminded that other investigators have observed that the passivation of GALFAN's corroded surface is greatly enhanced by its corrosion products. This paper indicates those products are Zn-Al hydroxides and that they migrate to the paint surface.
Leroy:	I agree with the observation but it does not explain why. I think the explanation is found in the wetting time. In the SST the humidity is 100% and the corrosion products are continuously washed, not giving any time for the aluminum hydroxide to form. It is evidence again that SST is not a relevant test for car bodies and many other coated applications. This is a problem for GALFAN and other coated products. We need to develop an accelerated corrosion test which is better correlated to outdoor corrosion. We need an effort for the building application similar to the efforts by the automotive industry's work with the Volvo test as proposed by Hoogovens et al.

Secondly, we have accelerated tests for automotive in which the ratio between actual exposure and accelerated test is 4 to 5 which is not too difficult because we have to develop a product with 6, 8 or 10-year guarantees, but for building applications, if we have only an acceleration factor of 4 and must guarantee for 20-30 years, I think we have a serious problem.

We should have a committee to develop an accelerated test for prepainted GALFAN building products.

Dubois: Can you tell me the Al content in the GALFAN coating and also, was there any Mg?

Kobavashi: Al is 5% and no Mg.

How far is the marine test site from the coast?

Kobayashi: 200 meters.

<u>Chairman:</u> It seems to me Mr. Leroy's suggestion that we explore the feasibility of developing an accelerated corrosion test which has correlation to corrosion in outdoor exposure is a good one.

<u>Celestin:</u> AISI has already started to develop such a test which would be applicable to any hot dip zinc or zinc alloy coating as used in the building industry.

<u>Dubois:</u> I hope the accelerated corrosion test you are talking about takes bending of the material into consideration. Testing plain flat panels does not give all the information needed.

A CORROSION RESISTANCE STUDY OF POST-WELDED BEZINAL® (GALFAN®) COATED WIRES.

M. Dewitte and P. Lippens

N.V. Bekaert S.A., Bekaertstraat 2, B-8550 Zwevegem, Belgium

1. INTRODUCTION

For many years, the GALFAN (eutectic 95 % Zn - 5 % Al alloy) coating on wire products has been shown to be very favourable with respect to corrosion protection. Application on wire products such as fishing ropes, vineyard wire, fencing, netting and many other products has resulted in a longer product life when compared with hot dip galvanising. [1]

The enhanced corrosion protection is due to the AI/Zn top layer and the Fe/AI(Zn) alloy layer which lasts a considerable amount of time longer, both in salt spray laboratory tests and during environmental exposure.

Recently, welded mesh was manufactured from pre-coated wires. Both Zinc coated and GALFAN coated wires were used. After a salt spray test, the metal bulges around the welding points show considerable rust in the case of the hot dip Zn coated wires, whereas in case of GALFAN no corrosion of the welding points occurs before the rest of the wire surface is corroded.

It is the aim of this work to demonstrate clear differences in the corrosion protection behaviour from galvanised and GALFAN coated wires/ wire products and to clarify the fundamental mechanism behind this enhanced corrosion protection for post-welded, GALFAN coated mesh. Therefore, a detailed analysis of the coating on the half product (before welding) is presented, followed by a thorough investigation of the welding points.

2. EXPERIMENTAL PROCEDURE

Drawn low carbon (0,08 % C) steel wires, of diameter 1.60 mm and 1.72 mm respectively, were coated with GALFAN in a double hot dip process. Polished cross sections of these wires were analysed with a PHI600 Scanning Auger Multiprobe (SAM) with an Energy Dispersive X-Ray (EDX) attachment : both surface Auger Electron-Spectroscopy (AES) analyses on the alloy layer and depth profiling, starting from the surface, were performed.

The GALFAN coated wires were also transformed into welded mesh. The 1.72 mm wire served as the line wire, while the 1.60 mm wire was used as the stay wire. After welding, samples of the mesh were imbedded, polished, etched with nital and inspected using an optical microscope. After selecting representative welds, the samples were broken from the bakelite and analysed with the SAM. Also AES-mappings were produced.

3. RESULTS

 A) Corrosion tests were performed in a salt spray test chamber according to ASTM norm B 117-85 ; a Kesternich test was also done (DIN 50018). Corrosion evaluation was performed both visually and by determination of weight loss. (See figs. 1 and 2). Furthermore, many corrosion comparisons were already realised in outdoor exposure circumstances. See table 1. B) Evaluation of the GALFAN coating composition on cross sections of the wire.

* Figure 3a is an optical micrograph showing part of a cross section through the GALFAN coating layer.

* Figure 3b is a secondary electron image (recorded in the SAM) of a cross section of a coated sample taken from the intermetallic alloy layer. In figure 3b and figure 3c the compositional variation through the alloy layer is indicated : the intermetallic alloy layer has a considerable enrichment in Al, with the highest concentrations occuring at the steel/GALFAN interface. At this interface, the coating consists of a nearly pure Fe/Al intermetallic with a small concentration of Zn. The enhancement in Al concentration and the depletion in the Zn is most clearly seen in the AES-mappings, figures 4a and 4b. This is in agreement with previous work [2].

* The composition of the metallic GALFAN layer in the surface area was characterised by depth profiling in the SAM starting from the wire surface. Figure 5 shows that the surface layers of the coating are enriched in Al. It is probably the pronounced affinity of this element to oxygen which causes the Al to diffuse to the surface layers during cooling down after the hot dip process. It was observed that in the AES depth profiles (fig. 5), the Al and O signals show more or less the same course.

C) INVESTIGATION OF WELDING POINTS OF GALFAN PRE-COATED MESHES.

A typical optical micrograph of a section through a weld is shown in figures 6a and 6b (detail). Of course, every weld spot has two bulges at each side of the wire. The detailed picture (6b) clearly shows that part of the bulge surface and of the wire surface near the bulge is no longer covered by a coating layer, but consists of uncovered steel which has to be cathodically protected by zones still coated with intermetallic alloy layer.

AES measurements were done on a number of weld cross sections in order to determine the exact nature of the phases being formed in the bulges and to identify the bright phase at part of the surface area from fig. 6b.

Figures 7a and 7b are AES-mappings showing the Fe-concentration and Alconcentration in a bulge. The Zn content in the bulge was not high enough in order to resolve it in an AES-map. However, it is clear that the tip of the bulge consists of a zone of approximately pure Fe, while at both sides of the tip the intermetallic Fe/Al alloy layer remains. Table 2 contains EDXpoint analyses and AES-point analyses on five indicated points of fig. 7c. The AES-analyses indicate for points 2, 3 and 5 an Al-concentration (approx. 20 %), which corresponds to the one in the intermetallic alloy layer as measured on the unwelded, coated wires (see fig. 3c).

In order to confirm this result, more welds were investigated and in this case EDX and AES-point analyses were made at regular distances all over the perimeter of the bulges. For each weld investigated, the bulge contained large areas with remaining intermetallic Fe/Al(Zn) alloy layer (see tables 3 and 4 and AES-mappings figs. 8 and 9).

4. DISCUSSION.

The presence of remaining Fe/AI(Zn) intermetallic alloy on some places of the bulges formed around the welds can be explained when considering the melting temperatures of these alloys. As the intermetallic phases in the system only contain small amounts of Zn, the composition and behaviour of the alloy will be close to the one for Fe-AI compounds such as FeAI2, Fe2AI5 and FeAI3. All these solid combinations have melting points above 1150°C (fig. 10) [3]. Of course, the introduction of small concentrations of Zn in the system will decrease the melting temperature of the latter, but it is quite clear that the overall melting temperature in most areas of the alloy layer is not lower than 1000°C, which is approximately the welding temperature.

This phenomenon is very favourable for the electrochemical corrosion behaviour around the weld. The distances from uncovered steel spots to remaining Fe/Al intermetallic alloy regions which protect the former cathodically will never be long : the current path for cathodic protection will be characterised by small resistances.

In case of a post-welded mesh consisting of pre-Zn-coated wires, the situation is completely different. Most intermetallic Fe/Zn phases (such as δ and ζ) have a melting point below 800°C (fig. 11), so that they will be completely melted away during the welding operation. Hence, the uncoated steel areas in the bulges will be larger and located much further from anodic areas.

Finally, it should be borne in mind that the electrical resistivity of an Fe/Al intermetallic layer will be lower than for an Fe/Zn intermetallic alloy. Also this is in favour of low resistance paths which give rise to better cathodic protection in case of welded mesh with a GALFAN coating.

5. CONCLUSIONS

The corrosion resistance of post-welded GALFAN coated wires is outstandingly much greater when compared with pre-welded galvanised mesh. Furthermore, it has been found that post-welded galvanised wire is very susceptible to corrosion at the weld zones of the mesh.

The exceptional corrosion resistance, of both the GALFAN coated wire and the weld zones, may be explained by the improved galvanic protection given by the entectic Zn/AI outer GALFAN layer and the corrosion barrier offered by the intermetallic AI/Fe(Zn) alloy layer at the steel/GALFAN interface. The remaining cathodic protection, given by the AI/Fe(Zn) intermetallic alloy layer at the weld zones, ensures that the welding process does not substantially degrade the corrosion resistance of the mesh (unlike post-welded galvanised mesh).

REFERENCES

[1] M. Dewitte, A.P. Van Peteghem and E. Wettinck : A new generation of corrosion protective coating, Wire Journal International, May 1990, pp 30 - 40.

[2] . F. Weinberg, M. Mager and L. Frederick: Segregation in Galfan hot dipped sheet steel, Canadian Metallurgical Quarterly, Vol 29, No. 2, 1990, pp. 163-166.

[3] L.F. Mondolfo, Aluminium Alloys : Structure and properties, pp. 538 - 540.

[4] M. Hansen, Constitution of binary alloys, Mc. Graw-Hill, 1958.

Table 1

In situ Exposure at Van Den Bergh, mink farm, Holland

Initial coating weight : Zinc

Zinc	:	± 300 g/m²
		(galvanized on welded mesh)
Bezinal	:	± 280 g/m²
		(pre-Bezinal coating on wire
		and welded afterwards)

Results after 4 years of exposure at the mink netting farm:

	Zinc (g/m²)	Bezinal (g/m²)	
Line Wire	39 - 0 - 108	132 - 148 - 122	
Cross wire	0 - 13 - 9	108 - 135 - 135	

Comments : The galavanized panel samples demonstrate 100% rust. The Bezinal panel samples are in good shape (dark, but smooth and clean).

T	8	b	e	2

EDX and AES point the welding b

Welgh	Welght %				
Point 1	AES EDX	4.40 4.12			
Point 2	AES EDX	0.52 9.75			
Point 3	AES EDX	0.16 4.79			
Point 4	AES EDX	0.00 6.61			
Point 5	AES EDX	0.07 4.63			

Та	h	A	R
	- 4	<u> </u>	

AES point analyses

	··	,	
Point Nr	Fe	Zn	Al
1	45.33	8.67	46.00
2	30.91	15.15	53.94
3	40.87	11.17	47.96
4	54.67	9.56	35.77
5	53.14	8.44	38.42
6	83.73	11.59	4.68
7	86.07	5.48	8.44
8	83.07	12.05	4.88
9	55.33	8.83	35.83
10	79.59	19.10	11.30
11	86.52	9.57	3.92
12	87.75	6.36	5.89
13	60.45	1.22	38.34
14	70.86	8.80	20.34
15	84.87	8.31	6.82
16	66.24	13.93	19.83
17	47.32	25.30	27.38
18	67.12	31.26	1.62

Table 4

AES point analyses

Point Nr	Fe
1	58.27
2	56.85
3	52.62
4	82.30
5	82.42
6	70.41
7	30.65
8	37.44
9	54.29
10	53.85
11	74.02
I	L

(data in wt%)









Fig. 3a: 560 X, optical micrograph of a cross section through a GALFAN coated wire, etched with nital.



Fig. 3b: Secondary electron image of part of a cross section through a GALFAN coated wire, recorded in the SAM after sputter cleaning during a few minutes.



Fig. 4a: Al AES-map of the GALFAN-steel interface (at the same place as fig. 3b).



Fig. 4b: Zn AES-map (at the same place as fig. 3b).



Fig. 6a: 60 X, optical micrograph of a section through a weld, showing line and stay wires, the heat affected zone and the metal bulges.



Fig. 6b: 270 X, detail of fig. 6a showing the bulge with a bright phase at part of its perimeter.



Fig. 7a: Fe AES-map of a weld bulge, showing the Fe depletion at part of the surface regions.



Fig. 7b: Al AES-map of the same place as fig. 7a.



Fig. 7c: Secondary electron image, recorded in the SAM of the same place as fig. 7a and 7b, showing the five spots where point AES and EDX analyses were performed (table 2).


Fig. 8a: Fe AES-map of another weld bulge.



Fig. 8b: Al AES-map of the same place as fig. 8a.



Fig. 9a: Secondary electron image of a third weld bulge. On the picture the 11 spots are indicated where the AES point analyses of table 4 were carried out.



Fig. 9b: Al AES-map of the same place as fig. 9a.





SECTION VI APPENDIX

QUESTIONS AND ANSWERS

Lerov:	I agree with your discussion concerning the Fe-Al alloy but I think it is related to your double-dip process. Do you agree?
<u>DeWitte:</u>	Yes. It is the reason we use the double-dip process. It makes a more efficient Galfan by transforming the galvanize alloy layer. What is surprising is that all of the alloy layer is transformed. The explanation must be the mobility of the aluminum.
Leroy:	We reach the same conclusion concerning the superior corrosion resistance of the intermetallics on sheet even though the Al enriched intermetallic is very thin. In crevice corrosion we observe that this thin intermetallic is very effective in protecting the steel. It is not exactly the same situation as you have but it does show the intermetallic compound to be very efficient.
<u>Capul:</u>	Do you have problems maintaining the aluminum composition in your Galfan bath?
DeWitte:	That is a good question. I am not going to answer in detail how we do this but we do monitor the Al and are able to maintain it between 4.8% and 5.5%. The operator must make accurate calculations because the double- dip process does carry a free zinc coating into the Galfan bath as well as the varying Zn-Fe alloy layer which is transformed into a 25% Al intermetallic. All these variables must be considered when selecting the Al composition of the make-up Galfan alloy.
<u>Gerenrot:</u>	You say the double-dip system is used to form an Al rich intermetallic but I understood it is used because you did not have good wetting (with single dip).
<u>DeWitte:</u>	That is true too. Wetting wire is even more difficult than sheet because of its low surface to mass ratio. Zinc will wet the steel much more easily than Galfan so the double-dip is an easy way to improve the reliability of the wetting.

SECTION VI APPENDIX

Chairman's Note

Early attempts to use electroflux to prepare wire for single dip Galfan coating were not consistent. Observations from the electroflux sheet trials at Wheeling-Pittsburgh and from the six operating electroflux tubing lines, it appears the earlier wire failures were due to inadequate cleaning. The electrofluxing process (like any electroplating) requires a much cleaner surface than hot dipping with less pure alloys.

We now think if electrolytic cleaning is used and dirt is reduced to $< .3 \text{ mg/cm}^2$, that wire can be Galfan coated with the single dip electroflux process.

BERGISCHE UNIVERSITÄT GESAMTHOCHSCHULE WUPPERTAL

(¿AUSS-STRASSE 20 POSTFACH 10 01 27 5600 WUPPERTAL 1 TELEN \$592 262 bughw TELEFON 102 021 439 - 1 TELEFAX (02 021 439 - 29 01



Fuchbereich 14 SICHERHEITSTECHNIK Werkstoffe und Korrosionsschutz Prof. Dr.-Ing. R. Nünninghoff

ILZRO GALFAN LICENSEES-MEETING October 13th to 14th 1992 Tokyo/Japan

Table of contents:

1 Galfan research 1.1 Introduction Different corrosion products of Zn, Al and Zn/Al (Zn-1.2 55-Al-1,6 Si) 1.3 Corrosion investigations with Galfan-coated wires Short-time corrosion tests in SO₂-atmosphere 1.3.1 Short-time corrosion tests in NaCl-atmosphere 1.3.2 1.4 SEM investigations with a micro-probe SEM investigations after short-time corrosion tests in 1.4.1 SO₂-atmosphere SEM investigations after short-time corrosion tests in 1.4.2 NaCl-atmosphere Electrochemical investigations 1.5 1.5.1 Equilibrium rest potential after SO₂-atmosphere testing Equilibrium rest potential after NaCl-atmosphere 1.5.2 testing 1.6 Conclusion 2 **Galfan** application 2.1 Wire ropes 2.2 Nails 2.3 Screws, rivets and small pieces 2.4 Welded wire mesh 3 Literature

<u>1</u> Galfan-Research:

1.1 Introduction

In the last few years, several investigations, made all over the world, could produce the evidence that Galfan-coatings have a 2 - 3 times better corrosion behavior or more in comparison to zinc-coatings as well in industrial environment (SO₂-atmosphere) as in rural or marine environment (NaCl-atmosphere). In addition, a much better adherence of the coating and a very high ductility are qualities of Galfan-coatings. But what are the reasons for the better corrosion behavior?

1.2 Different corrosion products of Zn, Al and Zn/Al (Zn-55-Al-1,6 Si)

Friel¹ and others could show after several investigations (long time corrosion tests in industrial, partly in rural and in marine atmosphere) that alumnium and zinc, as well as a Zn/Al-coating (Zn-55-Al-1,6 Si), are building totally different corrosion products, each with different behavior.

The corrosion products of zinc-coatings have always a crystalline structure (e.g. hydrozincite $Zn_5(CO_3)_2(OH)_6$ and zinc oxide ZnO). The principal product found on the surface of aluminized and Al/Zn-coatings (Zn-55-Al-1,6 Si) was amorphus Al sulfate hydrate (respectively Al Zn sulfate hydrate). In marine environment the Al-coating and the Al/Zn-coating (Zn-55-Al-1,6 Si) also formed Al(OH)₃, which is amorphus, too.

The crystalline corrosion products of the zinc-coatings are washed out in the course of time. The amorphus corrosion products (e.g. Al sulfate hydrate) of the Al-coatings and the Al/Zn-coatings (Zn-55-Al-1,6 Si) have a very good adherence in both environments (industrial and marine atmosphere). So, they are not washed out easily.

The Al/Zn-coating (Zn-55-Al-1,6 Si) consists of Al-rich dendrites and Zinc-rich interdendritic regions. With longer corrosion endurance the former Zinc-rich interdendritic regions are partly washed out and filled

with AlZn sulfate hydrate. The portion of Zn of this AlZn sulfate hydrate decreases significant under corrosion conditions in the course of time.

1.3 Corrosion investigations with Galfan-coated wires

To examine the corrosion mechanism of Galfan-coatings, several investigations were made at the Bergische University of Wuppertal (Germany) in the last months. Short-time corrosion tests according to DIN 50 018 KFW 2,0 S and DIN 50 021 SS have been made with standard Galfan-coated wires.

1.3.1 Short-time corrosion tests in SO₂-atmosphere

Respectively 3 specimen were taken away after 1, 2, 5, 10, 15 and 20 cycles SO_2 -atmosphere testing. Each specimen was devided into two parts. One part was embed in a cross-microsection for further SEM investigation with a micro-probe, the other part was needed for measurement of the equilibrium rest potential.

1.3.2 Short-time corrosion tests in NaCl-atmosphere

After a corrosion endurance of 24, 48, 120, 250 and 500 hours, each 3 specimen were taken away from the corrosion test and divided into one part for cross-microsection and the other part for electrochemical investigations.

1.4 SEM investigations with a micro-probe

To look what happens in the microstructure of Galfan eutectic under corrosion conditions in SO_2 -atmosphere and in NaCl-atmosphere, several investigations with a SEM in connection with a micro-probe have been made at the ARBED Recherche in Esch/Luxembourg.

The aim of the investigations was to find changes in the distribution of the chemical elements Fe, Al, Zn and O over the coating thickness in

dependence of the corrosion endurance. The following results (figures 1 - 10 and diagram 1 - 7) are to be regarded as a pre-publication of a doctoral dissertation of Volker Hagebölling at the Bergische Universität Wuppertal, Germany.

1.4.1 SEM investigations after short-time corrosion tests in SO₂atmosphere

The eutectic texture of the uncorroded Galfan-coating is to be seen in Figure 1 (optical photographie) and 2 (SEM photographie). Diagram 1 represents the standard distribution of a Galfan-coating: An alumnium portion over the whole layer with an average of about 5 - 7 %, increasing a the transition to the steel. The Fe portion decreases with further distance to the steel from about 99 % to about 0.5 - 1 %. The Zn portion ranges about 95 %. Oxygen can not be proved.

Already after 2 cycles of SO_2 -atmosphere testing a change of the distribution of the investigated elements is clearly visible. At the corrosion front the element Zn decreases significant to values of about partly 60 % as in the same way alumnium increases to values of about 15 - 20 %. Additionally Oxygen can be proved in portions of about 4 %.

This development at the corrosion front, the decreasing of zinc and the increasing of alumnium, in connection with an increasing of oxygen at the same locations, gets stronger with longer corrosion endurance. After 10 cycles SO₂-atmosphere testing, the coating thickness has decreased (cf. fig. 3 and 4). The distribution diagram (cf. diagram 2) shows a significant increase of alumnium and oxygen. The portion of zinc has decreased down to less than 50 % over a distance of nearly 20 μ m from the corrosion front. The alumnium values ranges between 20 and 25 % in the same area. Oxygen reaches values of about 15 - 20 % at the alumnium-enriched locations.

After 15 cycles SO₂-atmosphere testing the decrease of the layer and the wash out of the zinc goes further on (cf. fig. 5 and 6, diagram 3). Nearly over the whole thickness of the rest coating (about 30 μ m) a decrease of

zinc can be noticed. The minimum rate ranges around 25 % at the corrosion front. On the other hand, a alumnium concentration of 25 % is proved over a distance of more than 30 μ m from the corrosion front. Oxygen increases in the same way and region to values of about 20 - 25 % as the alumnium increases.

Over the whole coating thickness $(35 - 40 \ \mu m)$, the value of zinc is less than 55 % already after 20 cycles SO₂-testing. The average value of alumnium is about 30 - 35 %, in peaks over 40 %. Oxygen reaches in peaks the same values of about 40 - 45 %, in average more than 25 % in a region, nearly 15 μm away from the corrosion front.

1.4.2 SEM investigations after short-time corrosion tests in NaClatmosphere

The structure of the texture and the distribution of the elements Fe, Al, Zn and O over the thickness of an uncorroded Galfan-coating was shown in figure 1 and 2 and diagramm 1.

Already after 48 hours NaCl-atmosphere testing a first enrichment of oxygen to values of 0,5 % can be proved. Alumnium reaches values of about 13 %, whereas zinc decreases to values of about 50 % at the corrosion front (10 - 15 μ m). The tendency of enrichment of oxygen increases with longer corrosion endurance. After 120 hours NaCl-atmosphere testing the value ranges between 12 and 20 % over a distance of 15 - 20 μ m. In the same way, alumnium reaches values of about 15 %, in peaks 20 %. The zinc portion decreases to values of partly 50 % over a distance of 30 μ m from the corrosion front.

After 250 hours NaCl-atmosphere testing the layer thickness has decreased (cf. fig. 7 and 8) and a significant enrichment of alumnium is proved over a distance of more than 50 μ m (cf. diagram 4). Oxygen reaches values of about 20 - 25 % over a distance of 25 μ m from the corrosion front. In the same region, the zinc values are about 50 % and further to the steel, they range between 80 and 90 %.

At the end of the tests (after 500 hours NaCl-atmosphere testing), the coating has reduced to only 50 - 60 μ m thickness (cf. fig. 9 and 10). A portion of oxygen of about 12 - 20 % (average) and 25 % in peaks is proved (cf. diagram 5). Oxygen can be found over a distance of 50 μ m from the corrosion front. The values of alumnium are ranging between 6 - 15 %. Zinc has decreased all over the coating (50 - 60 μ m) and the values are lying between 50 and 90 %.

1.5 Electrochemical investigations

To corroborate the SEM investigations with the enrichment of alumnium and oxygen at the corrosion front with longer corrosion endurance, electrochemical measurements of the eliquilibrium rest potential were made with the second parts of the corrosion test specimen and specimen, taken away after 25 and 30 cycles SO₂-testing respectively 750 hours NaCl testing, in 0,01 n H₂SO₄.

The aim of these investigations was to show the change of the equilibrium rest potential of the specimen in dependence of the corrosion endurance. The enrichment of alumnium oxid at the corrosion front, which is relatively electropositive in comparison to the steel, zinc and its corrosion products, must lead to a change of the equilibrium rest potential to more electropositive values.

The equilibrium rest potential of the uncorroded Galfan-coating in 0,01 n H_2SO_4 (pH =2,46) is -762 mV (all values are measured versus NHE). The changing of the potential in depence of the corrosion endurance is shown in diagram 6 (after SO₂-atmosphere testing) and in diagram 7 (after NaCl-atmosphere testing).

1.5.1 Equilibrium rest potential after SO₂-atmosphere testing

The equilibrium rest potential changes from -762 mV (uncorroded) to -778 mV after 1 cycle and to -779 mV after 2 cycles. Then the values increase continual to -718 mV after 30 cycles SO₂-atmosphere testing. This means a change of the equilibrium rest potential of more than 40 mV. The gradient of the potential curve is relatively equal and positive during the last 20 cycles, so that a change of the equilibrium rest potential to more positive values can be expected with longer corrosion endurance.

1.5.2 Equilibrium rest potential after NaCl-atmosphere testing

Already after 24 hours NaCl-atmosphere testing the potential values decrease to -773 mV (cf. diagram 7). Then a change to more electropositive values can be observed. Finally, after 750 hours NaCl testing, the equilibrium rest potential amounts to -751 mV. The gradient shows continual positiv values, so that a continuous change of the potential to more positive values can be expected with longer endurance of corrosion.

The galvanic activity of the corroded Galfan-coating has become greater and so the tendency to go into solution (to corrode) is much smaller. This trend could be proved as well in SO_2 -atmosphere as in NaCl-atmosphere. The values under NaCl-atmosphere are not so significant, but it should be noticed that the relatively thick NaCl-layer on the surface of the specimen affects the electrochemical measurement. To corrode this coating, more external energy is necessary. Under equal corrosion conditions the corrosion rate gets less the longer the corrosion continues.

1.6 Conclusion

These results corroborate former results with just new manufactured Galfan wires. After about 1 year seasoning in the laboratory the equilibrium rest potential changes to more electropositve values. These behavior has never been found on zinc-coatings. So the change of the equilibrium rest potential must be connected with the enrichment of alumnium and oxygen at the corrosion front.

Diffusion of alumnium cannot be the cause for this phenomenon because of the necessary very high diffusion rate (more than 40 μ m in only 250 hours at a temperature of less than 40 °C), which is physical and chemical impossible.

The Galfan-coating consists of a eutectic texture with 95 weight % Zn and 5 weight % Al (and traces of rare earth). So there are great Zinc-rich regions. With longer corrosion endurance the former Zinc-rich regions are partly washed out and filled with AlZn sulfate hydrate (SO₂-testing) respectively with alumnium hydroxide (NaCl-testing). The washing out of non-adherent zinc oxidation products, due to their crystalline structure, in connection with the filling up of the dissolved former zinc-rich regions with amorphous alumnium (Zn) oxid products, seems to lead to the proved enrichment of alumnium and oxygen, and the decrease of zinc at the corrosion front. The portion of Zn of this AlZn sulfate hydrate (SO₂-testing) probably decreases under corrosion conditions in the course of time. Further investigations are at work.

According to the above mentioned results, the enrichment effect is much greater at Galfan-coatings as at Zn/Al-coatings (Zn-55-Al-1,6 Si) of former investigations. The much higher portion of zinc with the corresponding higher washing out rate under corrosion conditions, seems to promote the enrichment of more electropositive alumnium corrosion products, although much less alumnium is in the coating. The electrochemical investigations prove this corrosion mechanism theory for Galfan-coatings. Carried on investigations to this theory with all its problems are running on at present at the Bergische Universität Wuppertal, Germany.

2 Galfan application:

2.1 Wire ropes

Nowadays, several radio masts in Germany and Scandinavia are rigged by Galfan-coated wires because of the considerable longer down time. Usual the rigging consists of a fully locked coil rope with two outer profilewires (Z-profile). A new application for such a fully locked coil rope is the Neckarstadion (Soccer Stadium) in Stuttgart, Germany.

The soccer stadium with place for more than 70.000 visitors gets now a new tent-roof construction (cf. sketch 1). It is the first time worldwide that such a big construction will be lodged by a Galfan-coated fully locked coil rope. The Galfan-coated wires were produced at the TrefilARBED Drahtwerke Köln in Germany.

To proof the quality of the Galfan coating of the Z-profiles, it was necessary to make a lot of SEM-investigations with a micro-probe and several metallographic investigations on cross-microsections. The SEMinvestigations have been made by the TrefilARBED Recherche in Esch/Luxembourg. The aim of the investigations was to show the total transformation of the Fe/Zn-alloy layer in a Galfan eutectic texture after the second dip at different locations of the Z-profil, each with different thickness of the Galfan-coating and structure.

The thickness of the coating is different at each investigated location due to the manufacturing process. Figure 11 - 13 show the crossmicrosections at the three different investigated locations. A typical Galfan eutectic texture is clearly visible at every position. The diagrams 8 - 10 show the line-scan of the distribution of the chemical elements Fe, Al and Zn (in %) over the thickness of the coating (in µm) at each of the three locations. Over the whole layer the part of alumnium ranges around an average of about 6 % or more down to the steel surface of the wire (cf. diagram 8 and 10). In some areas the value increases to nearly 12 % alumnium (cf. diagram 9). The part of iron (Fe) ranges between 15 % and 2 %. The results of the SEM-investigation with the micro-probe produce the evidence that alumnium of the Galfan alloy (second dip) has diffused through the Fe/Zn-alloy (first dip) down to the steel surface of the wires. So, however, the whole coating of the profile-wires (Z-profile) consists only of Galfan eutectic.

2.2 Nails

In several fields of industry magazine nails, automatically shot by compressed air, are used. Necessary for this application is a very smooth surface of the nails.

Because of the more and more getting worse of the environment due to a more agressive atmosphere, the trend goes away from the electrogalvanized (piece) nails (about 5 μ m coating thickness) to the hot-dip galvanized nails (piece) (about 50 μ m coating thickness). But it is impossible to get an equal smooth surface by use of the hot-dip galvanizing process. Another problem of this manufacturing process is the bad adherence of the brittle Fe/Zn-alloy. So, after mechanical stress and strain (e.g. hit with a hammer on the nail), often the zinc-coating bursts away locally.

A solution of the problems of bad environmental conditions and the rough and brittle Fe/Zn-alloy in connection with the relatively bad adherence is the use of the Galfan-coated CRAPAL-nails of the TrefilARBED. These nails are manufactured of Galfan-coated wire by transformation of the <u>coated</u> wire into nails. So, due to the manufacturing process, the head and the top of the nails have no corrosion protection. But the surface is totally smooth and the Galfan coating has a well known ductility and adherence. Mechanical stress and strain, as they could arise by the use of magazine nails, are no problem for this coating with its very high ductility. Consequently, Galfan-coated nails are best suited for the use as magazine nails and others.

To show that Galfan-coated nails have a better corrosion behavior than zinc-coated or other coated nails, although the heads and pins have no corrosion protection. several investigations with different coated nails have been made in the last 6 months at the Bergische Universität Wuppertal, Germany. All tests were short-time corrosion tests according to DIN 50 018 KFW 2,0 S and DIN 50 021 SS.

The first investigation we have made, was the direct compare of zinccoated and Galfan-coated nails. Figure 14 shows the heads of the starting material, figure 15 shows the shafts and pins of the starting material (No. 7 and 11 are zinc-coated and No. 8 and 12 are Galfan-coated). After only 15 cycles SO₂-atmosphere testing all zinc-coated nails were corroded, as well at the heads (cf. fig. 16 No. 7 and 11) as at the shafts and pins (cf. fig. 17 No. 7 and 11). Although the Galfan-coated nails have no corrosion protection on the head and at the pin due to the transformation process of the Galfan-coated wires, they show no corrosion attack all over the surface (cf. fig. 16 and 17 No. 8 and 12). The same results we have got by tests with different sizes of nails and by salt-spray testing (according to DIN 50 021 SS).

Another investigation we have made with all the usual offered nails, which do have naturally different coatings: Dacromet A and B, galvanized, sherardized, aluminized, hot-dip galvanized, zinc-sherardized and Galfan-coated. Figure 18 shows the heads of the starting material of the following investigated nails: Dacromet A (Cr^* A), Dacromet B (Cr^* B) galvanized (el. Zn) and sherardized (Shera). Figure 19 shows the shafts and pins of the same nails. After only 15 cycles SO₂-atmosphere testing all specimen were corroded all over, partly heavily (cf. fig. 20 and 21).

The short-time corrosion test in SO_2 -atmosphere with aluminized, hotdip galvanized, zinc-sherardized and Galfan-coated nails (cf. fig. 22 and 23) results in the same view: after 15 cycles all specimen were heavily corroded with the exception of the Galfan-coated nail (cf. fig 24 and 25). Although the head and the pin are without corrosion protection, the corrosion behavior is better than that of the other coatings.

The good corrosion behavior at the critical locations of head and pin can be explained by the good distant effect of Galfan. Surely this distant effect is not endless. At present several investigations are made at the Bergische Universität Wuppertal, Germany, to find out all coherences of the coating thickness, the diameter of the nail heads and the distant effect.

Concluding one can say that Galfan-coated nails have several advantages in comparison to nails with other coatings:

- * The Galfan-coating has an excellent adherence at the wire due to the absent of an brittle Fe/Zn-layer. So it is possible to transform it without damage of the surface.
- * The manufacturing of the Galfan wire in a line production results in a totally equal surface of the coating. Thickenings, as usual by the piece-coating with zinc, disturb by the use as magazine nails (automatically shot by compressed air).
- * Due to the distant effect the non protected locations as heads and pins are protected against corrosion for a very long time, too. Because of a lower corrosion rate and the distant effect, Galfan-coated-nails have a significant longer life-span as zinc-coated nails.

So, Galfan-coated nails made of Galfan wire are excellent suited for the use as magazine nails due to their uniformity, their very good adherence and the much better corrosion property.

2.3 Screws, rivets and small pieces

For months we have made a lot of trials with our industrial partner in the south of Germany to develop a new manufacturing process for hot-dip galvanizing with Galfan-coating for high resistant screws, rivets and other small pieces. After first steps with a little testing plant, the trials could be continued with a special for this case new built Galfan vessel under production conditions with much success. At present, a reworking of the cooling system and the operational efficiency of the centrifuge is in preparation. The principle process parameters under production conditions have been worked out in many trials. All problems seemed to be solved aside the centrifuging and parts of cooling. We think that the starting of production of Galfan-coated high stress resistant screws, rivets for construction of vehicles and other small pieces is possible in spring 1993.

An example for the great progress during the investigations is to be seen in figures 26 to 31 and diagram 11 and 12. After the hot-dip galvanizing (first dip, cf. fig. 26 and 28) a typical, relatively spiky zinc-texture is to be seen. During the second dip (Galfan-coating), only in a short time, the zinc-texture is totally transformed into Galfan-eutectic (cf. fig. 27 and 29). The required layer thickness is also present.

The figures 30 and 31 in connection with the diagrams 11 and 12 produce the evidence that the whole spiky zinc-layer is total transformed into a Galfan-coating. The alumnium has diffused through the whole layer down to the steel. Consequently, the coating of the piece-coated high resistance screws consists only of Galfan-coating.

2.4 Welded wire mesh

Over the past years, systematic tests have been carried out on welded joints of Galfan-coated surfaces in comparison to zinc-coated welded fences and wire meshs. The results are conclusive (cf. my report at the ILZRO GALFAN LICENSEES MEETING in Liège 1990): if the welding electrodes and the voltage are adjusted to the Galfan-coated surface, a welded joint between such surfaces is possible and the positive anticorrosion properties remain unchanged.

Several investigations in Italy and Germany show the very good corrosion behavior of welded Galfan wire mesh in comparison to zinc-coated wire mesh. Short-time corrosion tests according to DIN 50 018 KFW 2,0 S have been made with Galfan-coated and zinc-coated welded fence (cf. fig. 32 and 33). The welded joint without corrosion protection layer of the Galfan-coated mesh is clearly visible (cf. fig. 33). Although there is no corrosion protection on the welding joint, the corrosion behavior of the Galfan-coated wire mesh after 35 cycles SO₂-testing is much better than that of the zinc-coated wire mesh (cf. fig. 34 and 35).

At present, the national institute EFIM in Milano, which is competent for the approval of materials used at the italian highways, has got the same test results with welded wire mesh and others (compare: zinccoated/Galfan-coated) as at the Bergische Universiät Wuppertal. Consequently, in Italy the tendency increases in using Galfan-coated wire mesh for gabionnades to wrap crushed rock in wire mesh and welded fence along the highways.

As far as products of this type are concerned, the results indicate two distinct advantages of Galfan in comparison to zinc, which have been confirmed by long-term practical applications.

Apart from the increased corrosion protection mentioned above, welded joints underline that Galfan offers a better distant effect than zinc. At the weld the coating is usually damaged down to the steel core and remains active only at the edges. Galfan, however, offers improved corrosion protection at the weld.

The higher ductility of Galfan in comparison to zinc-coated (i.e. piececoated) fences has to be mentioned at this point. Consequently, cracking under mechanical strain is not to be expected. Furthermore, buckling which is possible under the influence of the temperature of molten zinc will not occur.

Therfore, the use of Galfan-coated wire in the production of welded fences does lead to an extended service life, as the disadvantages of zinccoatings, such as buckling and cracking, are no longer significant.

3 Literature

1) J.J. Friel, CORROSION - NACE, Vol. 42, No. 7, July 1986, page 420 - 426














































 500 ± 1



500:1

Prof. Dr.-Ing. R. Nünninghoff Universität Wuppertal

NEW RESULTS IN GALFAN RESEARCH

Fig. 29:

Total transformation of the zinc-texture (cf. fig. 28) into Galfan eutectic during the second dip; high stress resistant screw: cross-microsection. edged

Typical zinc-layer of a hot dip

Fig. 28:

galvanized high stress resistant screw: cross-microsection, edged









Fig. 34: Zinc-coated welded fence (25 x 40 mm) after 35 cycles SO2-atmosphere testing with locally heavy corrosion of weldings the wire



Fig. 35: Galfan-coated welded fence (25 x 40 mm) after 35 cycles SO2-atmosphere testing; no significant corrosion attack of weldings and wire

Prof. Dr.-Ing. R. Nünninghoff Universität Wuppertal

NEW RESULTS IN GALFAN RESEARCH

QUESTIONS AND ANSWERS

Parrish:	Referring to the corroded nails 7, 8, 11 and 12 (Fig. 14-17) which compared the corrosion resistance of GALFAN with regular galvanized, was the regular galvanize coating electrogalvanized or hot-dipped?
Nunninghoff:	Hot-dipped.
Parrish:	Did you do any corrosion tests after hammering on the head?
Nunninghoff:	Yes. The results shown, however, are without hammering. With hammering, corrosion is severe after 5 cycles in SO_2 but GALFAN is still superior. Remember, the GALFAN nail is made from coated wire and there is no coating on the head and point but these figures show no corrosion.
Chairman:	Do you think there is any significant "smear" of GALFAN on the newly- exposed surfaces when the wire is cut?
Nunninghoff:	Yes. A little. But it is mainly the cathodic feature which protects the head and the point. There is of course a maximum head diameter beyond which the GALFAN will not protect the center. We are carrying out experiments to determine what the maximum diameter is.
Stoneman:	Can you tell us the coating thicknesses for the nails in these investigations?
Nunninghoff:	Yes. Both coatings are about $300g/m^2$ (45 microns thick).
Leroy:	What is the steel base quality used in these nails?
Nunninghoff:	All are made from mild steel.

Section VII—Appendix (cont'd.)

Leroy:	I understand you have a two-dip process for GALFAN coating these nails.
Nunninghoff:	Yes. The wire is first hot-dipped in a regular all-zinc and then in the GALFAN bath.
	Did you say that GALFAN coated small parts are now available in Germany?
Nunninghoff:	Yes.
	Are these parts done with two-dip process?
Nunninghoff:	Yes.
<u>Pelini:</u>	Did you identify the corrosion structure? Did you study the effect of the Al oxides on the corrosion mechanism, rate of corrosion, etc.?
Nunninghoff:	No. Not yet. This is the first report.
Gerenrot:	What was the surface preparation of the wire before the double-dipping process?
Nunninghoff:	The normal zinc-ammonium chloride fluxing.

GALFAN / ALUMINUM-RICH PAINT COATING SYSTEM FOR WELDED STEEL AUTOMOTIVE TUBING

Ronald V. Lebeck, Handy and Harman Automotive Group John D. Hostetler, Decktec, Inc.

Introduction

Small diameter welded automotive tubing is made from annealed cold rolled low carbon steel strip. The strip is roll formed and continuously welded into a tubular shape. The weld flash is removed by a scarfing process after the welding operation and the tubing is then directed into a multi-stand rolling system which precisely reduces it to the final outside diameter. Most small diameter tube mills have the capability to produce O.D. sizes from 3/16 to 1/2 inch diameter with wall thicknesses from .020 to .065 of an inch. In addition, most tube mills in the United States now have the capability to produce popular metric sizes. Most of the small diameter welded tubing used by the automobile industry goes into fabricating the following products:

- Fuel Tubes
 - Pressure Lines
 - Vapor Lines
 - Return Lines
- Transmission Oil Cooler Tubes
- Vacuum Tubes
- Power Steering Tubes
- Engine Tubes
 - Dipstick Tubes
 - Fuel Rails
 - Air Tubes (Emission System)

Introduction (*cont'd*.)

The tubing used by the automobile industry may be used as a single piece or installed on a vehicle as a complete bundle or "cluster". Bundles may not only include different types and sizes of tubing but also wire and cable harnesses and assemblies.

Low carbon steel tubing for automobiles is generally used in applications where the inside diameter does not need protection from the fluid or atmosphere inside. The outside of the tube however, may be subjected to the corrosive elements of the exterior environment.

Prior to 1980 external corrosion protection for U.S. automotive tubing was minimal. Terne (lead/tin alloy) was used in several different coating weights ranging from 0.06 oz/ft^2 (18 g/m²) to 0.16 oz/ft^2 (49 g/m²) to protect the tube surface. This coating provided about 24 hours of salt spray protection (per ASTM B117). After 1980, a secondary coating of zinc-rich paint was used over the terne to extend the corrosion resistance of the tube. This duplex coating increased the minimum corrosion protection of the tube to about 240 hours of salt spray. All three U.S. domestic car manufacturers currently use this product on a majority of their vehicles.

Pressures to extend the corrosion resistance of the total vehicle have prompted U.S. automotive manufacturers to specify a new duplex coating which can extend corrosion resistance to over 3,000 hours of salt spray. The new duplex coating consists of a layer of Galfan® at a minimum of 0.12 oz/ft^2 (38 g/m²) applied over the low-carbon steel tube surface and then top-coated with .03 oz/ft² (9 g/m²) aluminum-rich epoxy paint. The new Galfan/aluminum-rich painted product provides at least ten times the corrosion protection of the previous terne/zinc-rich painted tube. The slight increase in product cost is outweighed by the tremendous increase in salt spray protection.

Currently there are nine tube coating lines in North America that are licensed by ILZRO to use the patented Galfan alloy. The following is a list of North American licensees:

Arc Tube, Inc. Bundy Corporation (2 lines) Caledon Tubing Handy & Harman Automotive Group, Inc. ITT Higbie Mfg. Co. (2 lines) Markin Tubing Pilot Industries

Introduction (*cont'd*.)

The technology and know-how to produce the Galfan/aluminum rich paint coating has developed rapidly as new lines have been designed and started up. This paper will discuss the generic process and equipment required to produce the new duplex coated tube. In addition, information on corrosion performance and current specifications will be included in this report.

PROCESS DESCRIPTION

Although tube coating lines are constructed as a series of individual processes they must be considered as a *total system* since all of the individual components interact as one. For the purpose of discussion the system will be divided into the three following sections:

(1) Tube Surface (Steel) Conditioning
 (2) Galfan Coating
 (3) Top Coating (Painting)

TUBE SURFACE (STEEL) CONDITIONING

The tube surface conditioning section must prepare the steel tube surface to accept the Galfan coating. The following elements make up this section:

- (1) Cleaning / rinsing
 (2) Pickling / rinsing
- (2) Flanter (1
- (3) Electro-fluxing
- (4) Drying / Preheating

Cleaning/Rinsing

The first step in surface conditioning is to thoroughly clean the surface. This operation must be designed to effectively remove *all* dirt, shipping oil, slight surface oxide (which may result from extended storage) and other surface residues that may be present as a result of the tube mill operation.

Cleaning/Rinsing (cont'd.)

The importance of properly cleaning the base tube surface cannot be over emphasized. All subsequent line operations are dependent upon its effectiveness. If the cleaning system is not effective, the pickling system will not adequately remove surface scale and oxides; if scale is not totally removed from the tube surface, the electro-flux operation will not be able to deposit a continuous layer of zinc which will cause a wetting problem in the Galfan bath, resulting in a defective coating. Incorrect techniques, inadequate or poorly designed equipment, and bad cleaning equipment maintenance can cause several types of coating defects. These defects include poor Galfan adhesion to the base metal, uneven coating thickness, and rough surface finish (especially along the weld seam).

Cleaning the tube surface prior to Galfan coating is not difficult if the proper equipment and methods have been selected. It should be noted at this point that the type and design of the cleaning equipment will be dictated by the type of plating/fluxing operation that is used. Experience has shown that the tube surface must be much cleaner than what is required for other hot dip coatings such as terne coat or regular galvanizing.

The type of cleaning solution used is another variable in the cleaning system. Most chemical manufacturers are able to determine the optimum cleaning solution for the system, but only if they test formulations on samples of tubing truly representative of the contamination and conditions normally found on the tubing to be coated. In addition, the supplier must analyze the hardness level of the water since this will determine the effectiveness of the cleaning solution. In most cases the basic alkaline cleaner must be complimented with builders, surfactants, and in some cases buffers (depending on the cleaning equipment construction) in order to perform optimally.

Simple immersion or high pressure spray cleaning is totally inadequate to prepare the tube surface for electro-fluxing. Even two-stage cleaning which includes mechanical brushing and high pressure rinsing has proved to be ineffective. This is not to say that the previous method cannot be used, but equipment *maintenance and chemical usage* necessary makes the them inconvenient and costly. The recommended cleaning system for an Electro-flux Galfan line is *high current density electro-cleaning*. In some cases a pre-cleaner will be necessary to prolong the effectiveness and life of the electro-cleaner. This is dependent on the condition of the incoming tube and throughput.

Cleaning/Rinsing (cont'd.)

Another process variable in the cleaning system is the *cleaning fluid temperature*. All sections of the cleaning system should have provisions for heating (with adjustable temperature controls) the cleaner and rinse solutions. The cleaning solution *strength* should be monitored by acid titration and adjusted often enough to maintain good statistical control. In order to minimize labor, the equipment's reservoirs should be large enough to require no more than one adjustment per shift.

Another consideration is the method of charging the cleaning system. Some companies may prefer to manually dump and reload the cleaning system in bulk after running the line a predetermined period of time or throughput Others may choose the preferred method which stores make-up cleaning solution off-line and continuously meters it into the cleaner reservoir so that there is constant but minimum overflow.

Even though a cleaning section may be capable of loosening or removing the oil, smut, and dirt from the tube, these loosened particles will have an affinity for the tube surface. To remove these particles and the residual cleaning fluid it is necessary to include a high pressure impingement type water rinsing system into the line. The same requirement applies to rinsing after the pickling operation.

Pickling/Rinse

Once the oils, smut, dirt, and residual cleaning fluids have been removed from the tube surface, it can be pickled to remove scale and oxides. The best results have been obtained, using a solution of hydrochloric acid and water. Once the optimum pickling *concentration* has been determined, it should be monitored by specific gravity and adjusted often enough to keep it under good statistical control. Another process variable is the *pickling solution temperature*. The pickling solution reservoir should be equipped with heaters and solution temperature controls since the solution temperature will influence its reactivity and effectiveness. Typical solution operating temperatures range from 105°F to 125°F (90°C to 100°C.)

Electro-Fluxing

Electro-flux is an ILZRO-patented process which makes it possible to apply a hot-dipped Galfan coating on a Cook-Nortemann flux type galvanizing line.

Since Galfan is purer and less reactive with steel than regular galvanizing or terme it will not wet the steel surface as readily. Adding Ce/La mischmetal increases the wettability of Galfan sufficiently for a heated reducing atmosphere process but it is not sufficient for cold flux systems. In addition, it is difficult to use fluxes designed for regular galvanizing, tin, or terme systems since chlorides in these chloride based fluxes will react with the aluminum in the Galfan to form deleterious aluminum chlorides. Two North American flux manufacturers, Ferro Technologies and Zaclon, add proprietary inhibitors to their fluxes to prevent this reaction.

There are three important transactions that take place during the electro-flux operation. The first is an almost instantaneous *chemical reaction* in which the free iron and iron oxides on the tube surface combine with chlorides in the flux to form iron chlorides and water. The second is an *electro-chemical reaction* in which zinc is electro-plated onto the tube surface. During the third phase the zinc-plated surface is *covered with a film* of electro-flux solution which prevents re-oxidation.

The pH of the solution must be maintained above 3.5 to prevent dissolution of the zinc. In order to produce satisfactory results and long life, the electro-flux solution should be circulated at a generous rate and passed through a filter which will keep iron contamination below 0.12% so as not to lose its wetting power. As in the cleaning and pickling systems, the solution temperature in the electro-flux section influences its activity so a temperature control system must be incorporated into the design of the electro-flux equipment. The activity of the solution should be monitored and periodically adjusted to keep it under acceptable statistical control.

Drying and Preheating

Proper precautions must be taken to assure the electro-flux coating on the tube is not burned to ash *before being immersed* in the Galfan bath. Secondly, if the flux film is not dried, the water in the flux will boil violently when it enters the molten Galfan bath creating an

Drying and Preheating (cont'd.)

undesirable turbulence that can deposit flux ash and dross on the tube surface. For this reason, Galfan coating lines must be equipped with flux drying and preheating.

In order to accomplish realistic drying and preheating parameters, the excess electro-flux solution must be removed from the zinc plated tube with an air blow-off system. The tubing can then be passed through a pre-heater which utilizes waste heat from the molten bath heating system to dry the electro-flux. Preheating the tube also lessens the amount of Galfan required in the bath, reduces residency time of the tubing in the bath, and lowers the heating input to the bath. It should be noted that the amount of preheating is limited to about 325°F (210°C). If this temperature is exceeded the flux may scorch and cause a defective coating interface.

The design of the preheater includes a dual chambered circular oven in which the hot burner flue gas is piped in one end of the chamber and out the other. The inner chamber wall becomes a radiant surface which dries the electro-flux solution and heats the tubing. Temperature control at this point is important and is accomplished by adjusting the diversion of hot flue gases entering the chamber.

Alternatively, the drying and preheating operation could be performed by using a high frequency induction coil system. Laboratory experiments have demonstrated the advantages of a variation of this process which completely rinses the electro-flux from the tubing and preheats it to approximately $800^{\circ}F$. (475°C) This allows the use of much smaller coating pots (both in size and heating capacity). In addition this process has the potential for reducing dross generation, increasing line speeds, and makes other new technologies such as ultrasonic coating more realistic.

GALFAN COATING SECTION

The Galfan coating section is the heart of the line. It must create the conditions which will result in the proper steel / Galfan interface and control the coating's thickness, profile, and

Galfan Coating Section (cont'd.)

metallurgical characteristics. For the sake of discussion this section will be divided into the following five operations:

(1) Coating Pot
 (2) Bath Heating
 (3) Coating Machine
 (4) Fast Freeze (Rapid Cooling)
 (5) Water Quenching

Coating Pot

Since molten Galfan alloy is extremely *corrosive*, traditional steel or iron pots should not be used. Even most stainless steel pots have relatively short lives, and can not be expected to provide more than one or two years life. For this reason most tube coaters opt for ceramic pots with high alumina content hot faces. The remaining portion of the ceramic pot has a cross section designed for molten metal crucible service with a cold face temperature of 150°F (115°C). A properly designed ceramic pot which is not misused or abused can be expected to have a service life of 15 to 20 years. The construction of a ceramic pot starts with a structural steel frame and a steel plate lining the walls and floor. Because there are many attachments of pipes, wire conduits, instruments, burners, pumps, etc. to the frame, it should be fabricated, inspected and painted at the manufacturer's facility. The gas-fired emersion heaters are installed and tested with the gas control panel before shipping the pot frame to the job site where the pot liner is then covered with a ceramic paper or board and the brick and castable ceramic installed and cured.

Curing the cast ceramic is critical. The immersion tubes can be removed from the heaters and, with precise schedules and careful techniques, the burners can be used for powering the cure cycles. Similarly, the burners can be used for the initial melt-down of the Galfan directly in the pot. These techniques and practices are important to protect the ceramic pot and provide an effective alloy melt-down.

Heating System

The Galfan bath is heated by one to three gas-fired nitride-bonded silicone-carbide tubes (rated 140,000 Btuh output each) about 8 inches in diameter and 36 inches (915 mm) deep. Immersion tube heating produces strong convection currents in the bath which keeps temperature gradients to less than 5°F top-to-bottom and end-to-end. Tube life and efficiency are increased by the use of a ceramic *turbulator* gas mixer in the tube. The burners are recuperative so that overall heating system efficiencies of 60% to 65% are common.

The gas, air, and electric controls for the heaters are housed in a NEMA 12 enclosure. The automatic control system includes appropriate flame supervision and other safety controls which are connected to the burners and tested together before shipping. Final adjustments are then made during start-up at the job site. The temperature is controlled by a microprocessor with a manual reset high temperature limit and an alarm signal on the low temperature limit. Turn-down ratios are set so that low-fire maintains the bath temperature set point at idle conditions.

Coating Machine

Tube coating lines should be designed so the tube passline is horizontally straight through the entire process section. This allows constant tension on the tube and reduces the chance of work hardening. The coating machine includes a long, narrow, deep box (trough) partially submerged at the front of the pot. The molten Galfan alloy is pumped into the trough until its metal level is higher than the passline and overflows back to the pot at each end. Since the trough sets above the molten bath, heat losses occur at the point of hot-dipping. For this reason it is necessary to operate the bath at 10°F to 15°F (5° C to 10°C) above the targeted hot dip temperature, which is approximately 850°F (505°C). It should be noted at this time that the pump consists of an air driven motor with water cooled bearings. The shaft, impeller, and housing are constructed of cast stainless steel in order to prolong their durability which is about nine months. Ceramic pumps which offer longer service life are also available.

When the tube exits the coating trough the Galfan coating weight is heavier than needed. The excess Galfan alloy is removed from the tube surface by a non-contact annular gas wiping knife which converts pressurized hot gas (usually nitrogen) to a thin jet which impacts the

Coating Machine (cont'd.)

circumference of the coated tube. The amount of Galfan removed is controlled by adjusting the static gas pressure in the wiping knife. Since the coating thickness is a function of line speed, an automatic system that monitors line speed and controls pressure has

been developed. All of the previous mentioned functions are controlled by the Air Wipe and Coating Control System (AWACCS).

The coating trough is located inside of a tight hinged enclosure which reduces heat loss and dross formation. In addition, the enclosure reduces the ambient temperature around the pot and eliminates dangerous spatter from the molten bath. Expanded mica pellets may be floated on the portion of the Galfan bath that is not covered by the enclosure to further reduces heat loss and oxidation.

Rapid Cooling

Rapid cooling is necessary to control the microstructure structure of the Galfan. A *eutectic* microstructure will maximize the formability and corrosion resistance properties of the Galfan. In order to assure this structure the Galfan must be *rapidly cooled* through its freezing at a rate of at least 60°F (32°C) per second. Achieving such a high cooling rate without affecting the surface finish of the Galfan coating requires thoughtful design of the equipment because excessive air velocities impinging on the molten Galfan surface can disrupt its smoothness and cause coating concentricity problems. It is very difficult to go directly from the gas knife to a water quench without adversely affecting the Galfan surface finish but a high volume of ambient air at a relatively low velocity can produce the desired cooling if a two-chambered design cooling tube which directs the air onto the tubing in a spiral diffusion pattern is used.

Water Quenching

After the tube surface has solidified it can be sprayed or immersed in water for final cooling. If subsequent pre-treat or painting operations are to be performed in-line it may be desirable to only partially cool the tube, since the residual heat may aid in further processing. Several types of heat exchanger systems can be used to dissipate heat from the quench water. The Galfan quench water may contain high enough levels of zinc and aluminum so that precautions must be taken to insure that the effluent is properly treated and/or disposed of. The

Water Quenching (cont'd.)

quench system should have adequate provisions to allow the control of the quench flow rate to maintain the predetermined temperature of the exiting tube. Since the evaporation rate of the quench is very high, it is recommended that an automatic water make-up unit be incorporated into the system reservoir.

TOP COATING/PAINTING

The paint system is the second component in the duplex Galfan / aluminum-rich paint system. The Galfan tube coaters generally consider their procedures for applying and curing the top-coat as *proprietary*, so no process details will be discussed in this paper. Technical details of the top-coat material are given on page VIII-15.

The painting section of the duplex coating line must first *convert and passivate* the Galfan surface to provide good adhesion to the substrate. Then it must coat and cure the aluminum-rich epoxy paint while assuring a smooth and uniform finish. In general, the top coating system contains the following four elements:

(1) Paint Pretreat
 (2) Paint Application
 (3) Paint Cure
 (4) Paint Cooling

ENVIRONMENTAL CONSIDERATIONS

Traditional tube coatings, terne, and terne / zinc-rich epoxy contain large amounts of lead. The elimination of these tube coatings in favor of Galfan / aluminum-rich epoxy paint will help eliminate lead from the workplace. In addition, the removal of lead from automotive tubing will reduce the amount of lead in the environment and make recycling easier and less expensive.

Over the past few years more and more pressures have been placed on industry to properly deal with industrial wastes. These pressures have come from a multitude of areas

Environmental Considerations (cont'd.)

which include federal, state, and local governments, environmental activist groups, and private individuals. For this reason, many companies worldwide have adopted policies which require proper handling and disposal of industrial wastes. As many companies have found out, disposal of industrial waste products can be very expensive. This, in turn, has prompted companies to seek new methods of reducing or totally eliminating processing wastes in order to reduce manufacturing costs.

The Galfan / aluminum-rich duplex coating line must consider several environmental areas albeit less severe than for previous coatings. The following list includes some of these but should not necessarily be considered complete.

- Alkaline cleaning solution (contaminated with dirt, iron, and shipping oil)
- Rinse water from the washing system
- Acid from the pickling tank
- Rinse water from the pickling tank
- Spillage from the flux operation
- Fumes from the pickle, flux, coating pot and heater operations
- Dross from the Galfan pot
- Galfan quench water (contaminated with Zn/Al alloy)
- Paint pretreat rinse water
- VOC emission from paint

PRODUCT PERFORMANCE

In general, Galfan / aluminum-rich paint coated low carbon steel tubing will provide over 3000 hours of salt spray protection (with no red rust) per ASTM B117 on an unscribed sample. Table One shows a comparison of salt spray results that can be expected from several types of tube coatings.

Product Performance (cont'd.)

Hours to Red Rust (ASTM B117)			
<u>Terne</u>	<u>Terne/Zinc Rich</u>	Galfan/Chromate	Galfan/Al-rich
24	240	360	3000+

TABLE ONE: Salt Spray Expectations

Damageability

Damage due to processing and/or handling tubing coated with the Galfan / aluminum-rich system is about the same as the current terne / zinc-rich coating and does not require additional tooling or special handling. It should be noted that other coatings such as PVDF coatings and zinc electro-plate / PVF topcoat require special packaging and procedures during processing, shipping and handling to prevent surface damage.

AUTOMOTIVE SPECIFICATIONS

The following automotive specifications have been written for Galfan/aluminum rich painted tubing in North America:

- General Motors Corporation: GM 123/124M (AGE)
- Ford Motor Company: ESA-M1A270-A and WSA-M21P26-A
- Chrysler Corporation: PS-8688 (Alum. Rich Organic Over Zinc Alloy)

In addition to meeting the requirements of the Galfan Specifications, North American automobile companies usually require that the fabricated tubing be subjected to vehicle performance testing. This means the component or assembly will be tested installed on a vehicle that will run either standard or corrosion durability tests. Once the tubing has passed all required testing, the tube coater will be placed on the company's Approved Source List.

CONCLUSION

- The synergistic corrosion resisting effect of some paint coatings on zinc coatings reported by ILZRO in 1982 is well-demonstrated by the duplex coating of Galfan® topcoated with Alrich epoxy. Typical performance of the system is 3,000 to 4,000 hours in an ASTM B117 salt spray test before the appearance of red rust.
- The Galfan alloy requires a cleaner tube surface than normally required for other hot dip coating processes. The required degree of cleanliness can be achieved with electrolytic cleaning. ILZRO's Electroflux surface preparation requires electrolytic cleaning method. Thus, electrolytic cleaning should be incorporated into the line.
- Current line designs can coat and paint up to 30 lb/minute or 300 FPM, whichever is least. New processes under investigation will likely increase the production rate to 45 lb/minute or 600 FPM, whichever is least.
- The coating and the processes are environmentally friendlier but the processes still require effective fume-scrubbing and wastewater treatment before discharge from the plant.



A Fabricated Tubing Cluster

Galfan's greater ductility allows the severe bending and swaging without compromising corrosion resistance. Some clusters are much longer and may include tubes carrying various fluids, wiring, hoses, filters, connectors, etc.

Coutersy: ITT Higbie Automotive



Section of Al-rich epoxy painted Galfan-coated steel tubing. 600x Courtesy: Cominco, Ltd.

MAGNI INDUSTRIES, INC.

2771 HAMMOND DETROIT MICHIGAN 48209

(313) 843-7855 TELEFAX (313) 842-6730

Date: August 1, 1992

TECHNICAL DATA SHEET

Product Description:

Dorrlflex G

Product Code:

Substrate:

Pretreatments:

Application:

% Weight solids:

% Volume Solids:

Weight/Gallon:

Dry Film Density:

Viscosity at 80° F:

Coating Weight:

Coverage:

Bake Schedule:

Reducing Solvents:

T92 (Silver)

Galfan, Galvanized, Galvalum

Chrome conversion, phosphatizing or degreased substrates only.

Flowcoat

45.0% minimum

32.0% minimum

9.3 lbs./gal. minimum

1.56

25 to 40 seconds on Ford #4

19.83 g/m² @ 0.5 mils

1027 sq.ft./gal. @ 0.5 mils

Inductive coil, Infrared, or Gas Fired Oven with parameters that will achieve proper curing and film thickness.

P.M. Acetate, Methyl Ethyl Ketone Based on different application requirements Magni Industries may designate alternate solvents or blends thereof to aid those specific processing requirements.

Shelf Life:	6 months	
-	Revised August 1, 1992	
	from January 17, 1991	pp. 101



VIII-17



OPERATOR'S SIDE VIEW

IMMERSION BURNERS IMPROVE GALFAN BATH HEATING



Developments in gas-fired ceramic immersion burners are benefiting aluminum and zinc processors. The ceramic tube immersion burner consists of a single close-ended outer tube, an internal recirculator tube, and a recuperative burner. They are particularly suited for the small wire and tube ceramic pots or for adding capacity to an existing pot without increasing the heat load to the kettle wall.

A new generation of gas-fired immersion tube burners, based on technology developed by British Gas in the 1970s, has found increased success over the past several years. Composed of silicon carbide, they are stable in molten aluminum and zinc, and have a high thermal conductivity.



Compared to conventional gas furnaces, operating costs are low and savings are substantial. High heat transfer coupled with the use of cost-effective natural gas as a fuel translates into energy savings of 20% to 70%, with fuel efficiencies exceeding 50%.

In the standard direct-fire reverberatory furnaces used for melting and holding of nonferrous metals, heat transfer is by convection or radiation, and the products of combustion come in direct contact with the bath. In the immersion tube, however, heat transfer is through conduction rather than radiation or convection. The tube operates at a temperature close to that of the molten metal, reducing oxidation and gas pickup and minimizing metal loss. The working environment is also improved and compliance with emission standards is facilitated.

Gas-fired immersion burners also offer temperature uniformity which improves dross and ash control. Immersion tubes have great operating flexibility. Because single burners or banks of burners can be operated independently, preventive maintenance can be carried out while production continues. Burners can be removed without shutting down production. VIII-20

SECTION VIII APPENDIX

QUESTIONS AND ANSWERS

I

Gerenot:	What problems have you had?
Hostetler:	Cleaning, especially along the weld line has been by far the biggest problem. We have found that when we rely on electrocoating in the electroflux process, we get superior results from electrocleaning.
Dubois:	I am not familiar with this system but I know that some tubing is copper plated for corrosion resistance. Could you explain the advantage of your system over Cu or Ni plated tubing?
Hostetler:	WE have only seen Cu coated tubing used in the refrigeration industry but none in automotive. Tubing used for brake lines is copper plated for subsequent double-wall brazing and there are now two lines applying GALFAN to those tubes. This paper limits its discussion to plain single- wall ERW tubing.
Dewitte:	What is the thickness of the zinc done by the electrofluxing?
Hostetler:	We aim for 0.5 micron (0.00002 inches) although good GALFAN wetting and coating is achieved with thicknesses much less than that.
Dewitte:	Do you get any kind of alloy layer with this process?
Hostetler:	The few micrographs we have had for study show no alloy layer at all. They look similar to what you would see on strip.
Dewitte:	What line speeds are you operating at?
Hostetler:	Most of the lines are designed for maximum line speeds of 90 MPM although a few are for 140 MPM. The limiting factor is usually the time required for curing the paint.

Section VIII—Appendix (cont'd.)

Dewitte:	Do you need a special atmosphere after electrofluxing?
Hostetler:	No. Usually the tubing is exposed to atmosphere before and after the preheating.
Leroy:	How critical is the preheating temperature before hot dipping?
Hostetler:	We try to raise the tubing to 125°C to 150°C to minimize the heating load in the pot.
Leroy:	Have you tried to coat high-strength steel?
Hostetler:	No. All the tubing is mild steel.
Leroy:	Have any of your customers had requirements to coat the inside of the tube?
Hostetler:	No. If you examine the samples being passed around, you will see the inside is clean (from annealing after welding) but not coated because the coating is applied after the tubing is formed and welded.
Blankenship:	Is all the tubing painted?
Hostetler:	Only a very small percentage is used without the top coat.

Influence of Resistance Welding Tip Geometry on Tip Performance in Welding Zinc Coated Steel

by

I

Ronald R. Solomon SCM Metal Products, Inc.

Anil V. Nadkarni SCM Metal Products, Inc.

Randall D. Clark SCM Metal Products, Inc.

prepared for:

17 th Galfan Licensee Meeting Keidanren-Kaikan International Conference Hall Tokyo, Japan October 12-14, 1992

ABSTRACT

Constant current welding tests were performed to investigate the wear characteristics of differing electrode materials and tip geometries when welding two types of zinc / zinc alloy coated steels. The purpose was to determine how the electrode material and geometry combinations affected weld life and electrode degradation when welding steels with significantly different zinc coatings. Electrode materials that were examined include Al₂O₃ Dispersion Strengthened Copper (GlidCop R) grades AL-60 and AL-25, Electrode geometries that were examined include the and Cu-Cr. pointed nose (A), domed nose (B), truncated nose (45°), and a modified pimple nose (G), all in the female design. The steels used in this study included Electrogalvanized Zn (EG) coated and Hot Dip Galfan^R alloy (Zn-5%Al/Mischmetal) coated steels. In addition, an upslope weld current schedule was also examined in welding tests with the Galfan coated steel.

This report deals primarily with the results obtained in performing weld tests with the Galfan coated steel. An additional report has been issued covering the full scope of this study, and was presented at the American Welding Society's Sheet Metal Conference V in October, 1992.

INTRODUCTION

Resistance spot welding remains a primary method for joining and assembling steel components in the manufacture of automobiles, appliances, and assorted products throughout the world. It is a versatile method that can perform quite ruggedly in the real world of process variation and consistently meet the demand for high quality weldments, while remaining a method that is relatively low cost.

Zinc and zinc alloy coatings, which are applied to steel for corrosion protection, make the resistance welding process more difficult to control due to the attack of the coatings on the electrodes. The zinc/alloy attack causes accelerated wear, which is defined or manifested in several ways, including mushrooming, brassing, sticking, surface burning, cracking, pitting, and eventual failure of the electrode to maintain current density for making acceptable welds.

It is the purpose of this paper to define the influence of electrode material and electrode geometry on electrode wear characteristics when welding Galfan coated steel using constant current, below expulsion welding conditions. The data presented in this paper is part of a much broader study that is an ongoing project at SCM Metal Products, Inc., to define electrode wear characteristics on a broad range of zinc/alloy coated materials. The following presentation deals with preliminary results on welding lobe development, electrode break-in characteristics, and constant current test results with respect to electrode material and electrode design when welding Galfan coated steel. This paper is supplemental to a more complete report on this data plus data generated for electrogalvanize coated steel that was presented at the American Welding Society's Sheet Metal Conference V.
TEST EQUIPMENT AND MATERIALS

The welding machine used in performing the tests in this study was a dual gun 2 X 70 KVA single-phase AC Taylor Winfield spot welder, with two Pertron ELF 2300 programmable controllers. Each gun operates separately from the other, i.e. separate transformer, controller, secondary cables, and pneumatic cylinders. Steel sheets are fed into the welding machine by a pneumatic, hitch feeder at an adjustable rate (up to 50 hits per minute).

The test matrix of electrode shapes, electrode materials, zinc coating types, and weld pulse schedules that was used for generating the data in this study is shown in SLIDE 1.

The test matrix included three types of electrode material, four types of electrode shape, and two types of coated material, totaling 24 combinations using the standard single pulse weld schedule. Six combinations of electrode shape and electrode material were tested using the upslope schedule with the Galfan coated steel.

The electrode geometries used in this study are shown in SLIDE 2, and included the RWMA A and B style tip designs, a 45° Truncated design similar to the RWMA E style, and a modified pimple design designated as a G style. All electrodes were 5/8" diameter, female, with a .250" diameter flat weld face.

The electrode materials used in this study are shown in SLIDE 3, and included Cu-Cr RWMA Class 2, GlidCop AL-60 RWMA Class 20, and GlidCop AL-25.

The coated steels used in this study are also shown in SLIDE 3, and included two types, one being electrogalvanized (EG) zinc coated, low-carbon steel, AKDQ, 70G70G, .032" thick, produced by National Steel Corporation, and the second being Weirkote Plus^R Galfan^R, hot dip Zn-5%Al/Mischmetal alloy coated low-carbon steel, AKDQ, GF-45, .036" thick, produced by Weirton Steel Corporation.

The weld pulse schedules used in this study are also shown in SLIDE 3, and included a standard single pulse schedule of 11 cycles, and the upslope pulse schedule which included a 6 cycle slope from zero to full current followed by 7 cycles of full current.

PROCEDURES

Welding test parameters were held constant as shown in SLIDE 4, with the only changes made from test to test being changes to weld current.

For each test in the matrix, a new pair of electrodes was set on the gun adaptors, and the alignment checked and adjusted. A carbon paper print was made for each electrode pair when proper alignment was achieved, and a weld lobe was developed. All steel sheets were wiped with a dry cloth prior to welding to remove any excess oil or loose contaminants. Weld Lobe development procedures are presented in SLIDE 5, and included starting the current at an expected no-weld level, making three hits, increasing current 500 amps, making three more hits, and so on until expulsion was clearly reached. Current was then decreased 500 amps, three hits made, decreased another 500 amps, three more hits made, and so on until a non-weld condition was once again reached. Peel tests were performed on the hits/welds at each current level, and the peel button dimensions (minimum and maximum) were measured and recorded. The peel button diameters were calculated as the average of the peel button dimensions recorded. This lobe development procedure was used as a means to document the changes that occur in current levels during electrode break-in, and how these changes might vary through the 24 combinations of the test matrix. Normally, 30 to 54 hits were made during this procedure. Based on the weld lobe determined going down in current, an approximate average of the expulsion current and minimum peel button (.22"dia. min.) current was calculated and chosen as the start run current for the constant current welding test. The electrodes used to develop the lobes were also used for the constant current test.

Constant Current Welding tests were then run, using the procedures as shown in SLIDE 6. Welding was begun using the start run current based on the lobe as developed per the above procedure. Peel tests were run on about the tenth weld of each test to verify the buttons met a minimum .25" diameter (average button dimensions) set-up weld diameter chosen for this test. Once set-up size was confirmed, weld current was held constant throughout each test, unless expulsion clearly occurred due to an extended electrode break-in period, or unless the first buttons produced were less than the aim set-up diameter of .25". When necessary, current was adjusted to eliminate either condition, then held constant through the balance of the test. Carbon paper imprints of the electrode faces were made after every 250 welds in the progression of each test, and peel tests were performed to verify and measure buttons at these same intervals. This procedure was continued until peel button diameters deteriorated to zero (no weld). The electrode life for each test was then determined using two different minimum buttons sizes as end of weld life criterion, .22", which was more reflective of the electrode face diameter of .25", and .16", which was more reflective of the steel sheet thicknesses. In using both criteria, weld life was defined as the last 250 weld test point that produced satisfactory buttons prior to two consecutive 250 weld increments that failed to meet the minimum weld button diameter.

Electrode weld face characteristics were determined based on the carbon paper imprints, the electrodes after test completion, and the weld surfaces of the steel sheets.

RESULTS AND DISCUSSION

The results of the tests performed in the test matrix are presented as averages by four separate groupings: electrode shape for Galfan data only, electrode material for Galfan data only, coating type comparing Galfan data to EG data, and weld pulse for Galfan data only. (Raw data for the individual tests is included in the more paper presented at the American Welding Society's Sheet Metal Conference V).

ELECTRODE SHAPE

SLIDE 7 shows the average results of the welding tests performed on the Galfan coated steel when the test results are grouped by electrode shape.

In general, the average weld lobes showed fairly consistent results in comparing the four electrode shapes. All 4 electrode shapes showed a downward shift in the minimum button currents and expulsion currents during the decreasing current portion of the lobe development procedure compared to the initial increasing current portion. This might possibly be explained by looking at the changes that occur at the electrode face during the very early stages of electrode wear (less than 100 welds). The basic changes that should be expected to occur are in face chemistry (contamination due to the zinc/alloy pick-up) and face geometry (distortion due to heat and pressure). Zinc/alloy contaminates the electrode material progressively with each hit of the electrodes. This contamination process changes the electrical and thermal properties of the electrode face, causing increased heat generation in the contaminated electrode face due to higher electrical resistance, and poorer heat transmittal from the electrode face/weld area to the electrode body due to the lower thermal conductivity. Assuming there is very little change in electrode face geometry during the early life of the electrode, which was confirmed in this study, these changes result in the tendency for the electrode face to run progressively hotter as the contamination increases, thus minimum button current and expulsion current tend to decrease during the lobe test procedure used in this study.

The constant current life results indicated that, on average, the electrode design that showed the longest life without sticking under this study's test conditions was the Truncated nose, followed by the A nose, and then the B nose. The G nose showed very good life results on two of three tests, but in the third test, the electrodes stuck to the test sheets and the test could not be continued. The life tests also showed that the truncated, A and B noses all welded at approximately the same final weld currents, while the G nose welded a currents much lower than the other three shapes, and much lower than the weld lobes would have indicated possible.

An explanation for these results is offered based on looking at the geometry of the electrode shapes as shown in SLIDE 8. As the electrodes wear during the life test, the electrode face diameters

tend to increase based on the electrode body shape. Increasing the weld face diameter leads to reduced weld current density and eventually inadequate current density to continue making satisfactory welds. In the most simplistic terms, the constant current life test is a measure of how many welds it takes for the electrode face to grow to the point that the current density decreases below that needed for acceptable welds. The generous radius of the B nose tends to increase the face diameter greatly as the electrode is worn, while the steep angle of the G nose tends to result in a much slower electrode face diameter increase as the face wears back into the electrode body. SLIDE 8 shows the approximate face diameters that each shape would have if .025" of material were worn away from the front end of each shape. A comparison of the geometric differences between each shape supports the results of the tests in this study, with the Truncated nose (@.30" worn face) expected to last longer than the A nose (@.31" worn face), which is expected to last longer than the B nose (0.35" worn face). However, the G nose (0.27" worn face) did not purely follow the results anticipated by this geometric relationship. As noted in SLIDE 7, the G nose experienced sticking on one of three tests, and the final weld currents were much lower than the other three shapes. This is explained by the observation that the electrode face diameters got smaller as the welding tests progressed rather than got larger. The outer edge of the electrode face of the G nose electrodes gave way, resulting in worn face diameters that were actually much smaller than the original .25" This required progressive reductions in weld face diameter. current to avoid expulsion and severe sticking until a steady run condition (reduced face diameter, reduced current) was established, as is evident in the low Final Weld Current values. The mechanism that appears to explain this observation would be the apparent mechanical instability in the G nose design. The outer edge of the electrode face has very little support and constraint provided by the electrode body, and simply failed due to the stress at the electrode face due to the weld pressure and elevated weld face temperature.

SLIDE 9 shows a microphotograph of the electrode face a G nose, CuCr electrode after less than 250 welds demonstrating the edge break-off occurrence that was seen in this electrode shape. The edge appeared to break-off at an approximate 45° angle, indicating a simple shear failure. It is noted this did not occur on any of the other three electrode shapes.

ELECTRODE MATERIAL

SLIDE 10 shows the average of results of the tests grouped by the three different electrode materials examined. On average, the lobe data for all three materials looked quite similar.

The life test results showed a tendency for the GlidCop materials to last longer than the CuCr material, with the AL-60 material showing the best overall average life results. This might be explained by looking at the higher high temperature strength characteristics of the GlidCop materials compared to the CuCr, which should resist electrode face wear and growth in the high temperature and pressure environment that the electrode face is exposed to during welding. Thus, weld face diameter should increase at a slower rate for the GlidCop materials, and current density levels for acceptable button diameters should be maintained longer.

Worth noting also was a tendency for light to medium sticking with the CuCr electrodes when in the expulsion portion of the lobe development tests, as well as sticking encountered on the G nose CuCr electrodes during their life testing. Neither GlidCop material experienced sticking, and this is believed to be due to the refractory nature of the aluminum oxide strengthening particles in GlidCop.

COATING MATERIAL

SLIDE 11 shows the average of the results when comparing the Galfan coated steel to the Electrogalvanize (EG) Zinc coated steel. The lobe data indicates that there was a tendency for the EG lobes to run at higher current levels than for the Galfan lobes. This might partially be explained in considering the bulk electrical conductivities (assumed) of the purer EG coating compared to the less pure Galfan alloy coating, with the purer EG requiring higher currents for weld heat to develop. Looking further into the life test data, however, it is shown that both coatings had Final Weld Current values approximately equal. This numerical observation supports the physical observations made during the performance of the tests that the EG steel required a longer break-in or adjustment period as the chemistry of the weld face appeared to change slower when welding the EG steel compared to the Galfan steel. For the EG steel, the higher start weld amperages as indicated by the lobes had to be eventually reduced to the same level as for the Galfan to avoid expulsion, but normally 60-150 welds into the life tests. The Galfan steels required essentially no current adjustments beyond the initial start weld currents in the life tests. This difference in break-in periods perhaps indicates that the chemistry of the Galfan alloy coating (5% Al/Mischmetal) affects the electrical and thermal properties of the electrode face faster than that of the purer EG, yet both reach the same end point as evident by the same Final Weld Currents once electrodes are fully broken-in. The Galfan coating thus leads to a quicker electrode break-in than the EG coating.

UPSLOPE WELD PULSE

The average results of the welding tests using the upslope schedule compared to the single pulse schedule are shown in SLIDE 12. The lobes for the upslope schedule followed the trend for decreased values on the decreasing current portion of the lobe test, but the currents were higher and the lobe ranges were much broader than for the single pulse schedule. Noting the upslope schedule used, 6 cycles up from zero to full current and then 7 cycles at full current, the equivalent 10 cycles of current spread over a 13 cycle timeframe was expected to require more current to develop the adequate weld heat when compared to 11 cycles of current in 11 cycles of time per the single pulse schedule. The wider lobe range for the upslope schedule appears to indicate that the upslope schedule provided more time at a lower heat condition for the electrode faces to more uniformly make contact with the steel sheets and distribute pressure to the weld area before the full weld heat was established. This should promote higher currents required for expulsion as localized overheating due to electrode face irregularities would be reduced, and uniformity in weld pressure at the sheet feying surfaces would be enhanced.

The life test results indicated that there was very little difference in the weld performance when comparing the upslope to the single pulse schedules.

CONCLUSIONS AND OBSERVATIONS:

SLIDE 13 lists the conclusions and observations made based on the data developed for the Galfan coated steel and reported on in this paper:

Electrode Design: -all 4 electrode shapes had similar weld lobes

-the Truncated nose had the longest dependable weld life results

-the G nose was prone to sticking and expulsion and required many adjustments due to electrode face edge break-off

- Electrode Materials:-the GlidCop AL-60 and AL-25 electrodes had longer weld life than the Copper-Chrome electrodes
 - -the Copper-Chrome electrodes were more prone to sticking than the GlidCop electrodes
- Coating Types: -the Galfan and EG coatings had similar lobes and weld life results, with EG lobes at currents slightly higher than Galfan lobes
 - -the Galfan coating promoted faster electrode break-in than the EG coating
- Upslope Schedule: -the upslope schedule required higher current and had wider weld lobes compared to the single pulse schedule, with comparable weld life results

RECOMMENDATIONS:

SLIDE 14 presents recommendations for welding Galfan coated sheet steel based on the data presented in this paper. It is recommended that the electrode used be the Truncated design made from GlidCop material, and both the single pulse and upslope pulse schedules be considered as viable alternatives, with the upslope schedule possibly providing a wider current range to operate in.

Test Matrix - Constant Current Testing					
Electrode Shape (Female)	Electrode Material	Coating Type			
A - pointed	GlidCop AL-60	Electrogalv. EG - pure Zn			
B - domed	GlidCop AL - 25				
Truncated -45°		Galfan			
G - mod pimple 20°	CuCr	Zn-5%AlMisch Hot Dip			

Examined on Galfan only: Single pulse vs Upslope For A and B nose only



Electrode Shapes

Electrode Materials					
Material	Composition Weight %	Hardness HRb	Conductivity % IACS		
GlidCop AL-60	1.1% Al ₂ O ₃ bal. Cu	82	78		
GlidCop AL-25	0.5% Al ₂ O ₃ bal. Cu	68	88		
Copper - Chrome	0.8% Cr, bal. Cu	75	80		

	Coating Type)S		
	Coating	Coating W	/t.	
Steel Description	Nominal	Nominal	Report	ed (top/bot)
			g./m. ²	oz./ft. ²
National EG .032"(.81mm) AKDQ, low carbon	Zn	70G70G	70/75	.23/.25
Weirton Galfan .036"(.89mm) AKDQ, low carbon	Zn + 5% Al + Mischmetal	GF45	82/64	.27/.21

Weld pu	lse schedule			
Schedule Current (60 Hz.AC)				
Single Pulse	11 cycles constant			
Upslope	6 cycles increase 7 cycles constant			

Weld Test F	Parameters			
Welding Force:	450 lbs.	2000 N.		
Minimum Button Dia.:	.22 in.*	5.6 mm.		
Aim Start Button Dia.:	.25 in.	6.4 mm.		
Weld Spacing, centers:	1.5 in.	38.1 mm.		
Squeeze Time: 25 cycles				
Weld Time:	11 cycles			
Hold Time:	5 cycles	5		
Off Time:	79 cycle	S		
Weld Rate, per minute:	30 welds	5		
Water Flow, per minute: at 75°F, +-5°	1.5 gal.	5.7 I.		
NOTE: 60 cycle, single pha	ase, AC curr	rent		
* weld life also determined	using .16"	(4.0mm)		

Lobe Test Procedures

- Start at No-Weld Current
- Increase Current to Expulsion
- Reduce Current to No-Weld
- Define Lobe Increasing & Lobe Decreasing Current



GlidCop AL-60 on Galfan with A-nose



SCM METAL PRODUCTS, INC.

Life Test Procedures

- Start at Current based on Lobe
- Adjust down only if EXPULSION
- Peel buttons every 250 welds
- Define life as 2 consecutive failures:

at .22"min. and at .16"min. button size

Life Test Results GlidCop AL-60 on Galfan with A-nose



RESULTS BY ELECTRODE SHAPE

For Weircote Galfan coated steel

	Avera	age Lobe Ch	aracter	istics		
Electrode Shape	Min. Butt. Increasing KA	Expulsion Increasing KA	Range Inc. KA	Expulsion Decreasing KA	Min. Butt. Decreasing KA	Range Dec. KA
A	12.5	13.3	.8	12.5	12.0	.5
В	12.5	13.0	.5	13.0	12.2	.8
Trunc	12.7	13.5	.8	13.3	12.2	1.1
G	12.8	13.7	.9	12.8	11.7	1.1
L	1]]]

Average Constant Current Life				
Electrode Shape	Final Weld Current KA	Weld Life Number of .22"min	Welds .16"min	
Α	12.4	1000	1420	
В	12.5	830	920	
Trunc	12.7	1580	1750	
G	10.3	2250-2 +1 stuck	2250-2 +1 stuck	



Electrode Shapes



G Nose - Weld Face Edge Break-off @50 X after 250 Welds

RESULTS BY ELECTRODE MATERIAL

For Weircote Galfan coated steel

	Average Lobe Characteristics						
Electrode Material	Min. Butt. Increasing KA	Expulsion Increasing KA	Range Inc. KA	Expulsion Decreasing KA	Min. Butt. Decreasing KA	Range Dec. KA	
GlidCop AL60	12.6	13.4	.8	12.8	11.9	.9	
GlidCop AL25	12.6	13.4	.8	12.8	12.0	.8	
CuCr	12.7	13.4	.7	13.3	12.2	1.1	

Average Constant Current Life					
Electrode Material	Final Weld Current KA	Weld Life Number of .22"min	Welds .16"min		
GlidCop AL60	12.3	1440	1875		
GlidCop AL25	12.1	1440	1440		
CuCr	11.9	1080 +1 stuck	1170 +1 stuck		

RESULTS BY COATING TYPE

Average Lobe Characteristics							
Coating Type	Min. Butt. Increasing KA	Expulsion Increasing KA	Range Inc. KA	Expulsion Decreasing KA	Min. Butt. Decreasing KA	Range Dec. KA	
Galfan	12.6	13.4	.8	13.0	12.0	1.0	
EG	12.9	13.7	.8	13.6	12.5	1.1	

Average Constant Current Life					
Coating Type	Final Weld Current KA	Weld Life Number of .22"min	Welds .16"min		
Galfan	12.0	1341 +1stkg	1523 +1stkg		
EG	11.8	1167 +1stkg	1500 +1stkg		

SCM METAL PRODUCTS, INC.

•

RESULTS BY WELD PULSE For Weircote Galfan coated steel

Average Lobe Characteristics						
Weld Pulse	Min. Butt. Increasing KA	Expulsion Increasing KA	Range Inc. KA	Expulsion Decreasing KA	Min. Butt. Decreasing KA	Range Dec. KA
Single	12.5	13.1	.6	12.8	12.1	.7
Upslope	13.2	14.4	1.2	14.3	13.0	1.3

Average Constant Current Life			
Weld Pulse	Final Weld Current KA	Weld Life Number of Welds .22"min .16"min	
Single	12.4	917	1167
Upslope	13.5	875	1125

CONCLUSIONS AND OBSERVATIONS

For welding Galfan coated steel using Constant Current, non-expulsion weld conditions:

- All electrode shapes had similar weld lobes
- The Truncated nose had the longest dependable weld life results
- The G nose was prone to sticking and expulsion, and required many current adjustments
- -The GlidCop Copper-Al₂O₃ AL-60 and AL-25 electrodes had longer weld life than the Copper-Chrome electrodes
- -The Copper-Chrome electrodes were more prone to sticking than both GlidCop Copper-Al₂O₃ materials
- The Galfan and EG coatings had similar weld lobes and weld life results, with the EG lobes at slightly higher currents
- The Galfan coating promoted faster electrode break-in than the EG
- The upslope weld current schedule had higher weld currents and wider weld lobes compared to the single pulse schedule, with comparable weld life results

Recommendations for Resistance Welding Galfan Coated Steel Using Constant Current, Non-Expulsion, Female, Flat face Electrodes, Non-Dressing:

Electrode Shape:	Truncated Nose	LONGEST DEPENDABLE LIFE
Electrode Material:	GlidCop® AL-60 or AL-25	NONSTICK AND LONG
Weld Pulse:	Single or Upslope	UPSLOPE MAY GIVE LONGER LIFE AND WIDER WELD LOBES

IX-24

SECTION IX APPENDIX

QUESTIONS AND ANSWERS

Dubois:	I would like to know the type of electrode you have used in these tests.
Solomon:	Four shape designs were used; pointed nose, B nose, truncated nose and G nose.
Dewitte:	Does the development of the gray patina have any affect on the welding?
Solomon:	I don't know.
<u>Chairman:</u>	How old were the GALFAN test pieces? Perhaps Weirton (who supplied them) can tell us.
<u>Celestin:</u>	We still have not seen the gray patina on our product. The material we supplied to SCM was several years old but there was no darkening.
Dewitte:	Do you use a treatment after coating?
Celestin:	Yes.
<u>Capul:</u>	Do you conclude that if the non-zinc alloy layer could be eliminated in regular hot-drip galvanizing (as GALFAN does) that it would weld the same as electro galvanized?
Solomon:	That testing will come later. We have not made these comparative studies on regular galvanize or galvanneal.
<u>Chairman:</u>	I'm looking for a reaction from the group. I was led to believe that welding GALFAN sheet was difficult and inconvenient; that it was a significant negative attribute. This report, however, says that the parameters are simple and convenient. Is that a safe statement?

<u>Solomon:</u>	It is a safe statement based on our tests which were run under expulsion. Our intention is to run additional tests at slightly above and below expulsion. We will be working with Weirton and Wheeling-Pittsburgh to test for life cycles using current steppers, examining changes in expulsion and button size after 8,000 to 10,000 welds and comparing more quantifiably at the incidence of sticking on various zinc coatings.
Leroy:	May I ask the extra cost for the Glidcop electrodes?
Solomon:	Generally about twice the cost of copper cone electrodes.
Leroy:	Have you discussed this price premium with auto makers?
<u>Solomon:</u>	About one-half of the automotive welding in the USA is done with Glidcop electrodes. They are used on regular galvanized, galvanneal and electro galvanized sheets.
Leroy:	I am surprised that the auto makers would use Glidcop at twice the cost.
Solomon:	The justification comes more from the reduction of sticking. I did not include the sticking occurrences in the average life of the electrodes. Had I done that, Glidcop would have appeared even better. I reported each incidence of sticking but a test was terminated if sticking occurred and not used to determine the average life.
<u>Parrish:</u>	Mr. Chairman, you asked for a reaction. The automotive and appliance markets in the USA are now using regular HD galvanizing, galvanneal, electro galvanizing and GALFAN. I think it is premature to draw conclusions about the weldability of GALFAN until it has been compared to all of the other coatings.
Dubois:	You show some difference in the life of Glidcop No. 25 and No. 60 when welding EG. Is there a similar difference when welding GALFAN?
<u>Solomon:</u>	We see a slight advantage of AL-60 over AL-25 in the smaller button size $(0.18")$. AL-60 is a stronger material, it is less prone to mushrooming, it tends to hold current density longer and does give slightly longer life.

Hiromitsu Fukumoto, Hisamitsu Mizuki, Masahiro Yoshino and Masatoshi Yokoyama

Presented by Hiromi Mashihara Nisshin Steel Co., Ltd.

NOTE: This Licensee adds 0.1% Mg in their Galfan Alloy (maximum allowable per ASTM B750). The surface pretreatment described herein has not been tested on Galfan without Mg.

A new acid-type surface conditioning treatment, as a pre-treatment for paint of Zn-4%Al-0.1% Mg alloy coated steel sheets, is a treatment that conforms to the pre-treatment philosophy (show in FIG. 1) by evaluation by the SVET.

And no sludge production was found after treatment of 185000 m² Zn coated steel sheets and 1500 m² Zn-4%Al-0.1% Mg alloy coated steel sheets by a new acid-type surface conditioning treatment in the pilot line. Because of Zn concentration of treatment solution does not exceed the solubility of Zn (45000 mg/l) at this state.

Keywords: surface conditioning treatment, Zn-4%Al-0.1 Mg alloy coated steel sheet, SVET, treatability, etching weight, Ni deposition weight, adhesion

1. INTRODUCTION

.

It is well known that when Zn-coated steel sheet is painted, without chemical surface treatment the paint film adhesion and corrosion resistance are poor, and performance as precoated steel sheet cannot be obtained. For Zn-coated steel sheet, a typical chemical surface treatment is to combine surface conditioning treatment and chromate treatment.

In chemical surface treatment, surface conditioning treatment has the role of electrochemically distributing anodes and cathodes on a Zn-coated layer surface in an appropriate ratio, causing a composite oxide film to form, and suppressing Zn overetching. This treatment is done in order to obtain a uniform coating of coating-type chromate film (FIG. 1-b).

Coating type chromate treatment serves as a binder for binding the Zn-coated steel and an organic coating by hydrogen bonding (FIG. 1-c).

And at GALVATECH '89 we reported the importance of surface conditioning treatment, showing that in precoating treatment of the surface condition of the Zn before doing a coating-type chromate treatment determines the performance of the coating-type chromate treatment.

Based on this way of thinking, for example, as a surface conditioning treatment, alkali-type composite oxidation treatment and as a chromate treatment, coating-type chromate treatment including silica sol or acrylic emulsion are used.

Alkali-type surface conditioning treatment has been used by many painting manufacturers because of its good paint film adhesion and corrosion resistance on painted Zn-coated steel sheet. But the alkali-type has the disadvantage that the Zn ion solubility into the treatment solution is low (2500 mg/l) and the treatment solution tends to produce sludge in which Zn is a major component. The generation of sludge not only lowers the treatability, but it is also known to cause after-coating paint defects when the sludge gets onto the surface of Zn-coated steel sheet.



To improve the quality of coated steel sheet, we studied treatment methods that produce little sludge, and attempted to apply acid-type surface treatments having a relatively high Zn solubility. This paper shows, by evaluation by the scanning vibrating electrode technique (SVET), that acid-type surface conditioning treatment, as a precoating treatment for Zn-4%Al-0.1%Mg alloy-coated steel sheet, is a treatment that conforms to the precoating treatment philosophy shown in FIG. 1. And this paper also reports on the state of sludge production during treatment of 185000 m² Zn-coated steel sheet and 1500 m² Zn-4%Al-0.1%Mg alloy-coated steel sheet by acid-type surface conditioning treatment in the pilot line.

2. PROPERTIES OF THE NEW ACID-TYPE SURFACE CONDITIONING TREATMENT

Table 1 shows the main components and properties of the treatment solution in comparison with a conventional alkali-type treatment solution.

The main component is hydrosiliconfluoric acid, and it contains Ni as a chelate metal. Its pH is controlled in the range of 3.5-4.5. The Zn solubility of the treatment solution is high, 45000 mg/l, which is 18 times that of the conventional alkali-type.

		a New Acid-type	a Usual Alkali-type
a main	a Solusion of S.C.T.	H ₂ SiF ₄	NaOH
Component	Metalic Ion	Ni	Co (Fe)
Properties	рH	3. 5~4. 5	13~14
	the Solubility of Zn	45000mg/1	2500mg/1
·····	(#S.C.T. Surface Con	ditioning	Treatment

Table 1 Characteristic of a New Acid-type S.C.T.

3. TREATABILITY OF THE NEW ACID-TYPE SURFACE CONDITIONING TREATMENT

Using the scanning vibrating electrode technique (SVET), we evaluated treatability of the solution as a surface conditioning treatment. The following shows an example of how surface conditioning treatments are measured by SVET.

 If the surface conditioning treatment is inadequate, a distribution of electric potential difference in which anodes and cathodes correspond is almost not detected. After this surface is given a coating-type chromate treatment for a short period of time and then is immediately rinsed with water, the places where a coating-type chromate treatment is formed become cathodes, and the places that did not react become anodes, and it is clear that a discontinuous chromate film is formed.
If an appropriate surface conditioning treatment is applied, a distribution of electric potential differences in which anodes and cathoder correspond is detected on the tested on the tested on the surface condition of the tested on te

differences in which anodes and cathodes correspond is detected on the treated surface, and after a coating-type chromate treatment is given for a short time, no anodes at all are detected. It is clear that a uniform chromate film has formed.

When the new acid-type surface conditioning treatment is applied to two kinds of zinc-coated steel sheet, the treatability for a Zn-4%Al-0.1%Mg alloy-coated steel sheet is high, and in a short time a surface having the necessary anode-cathode distribution is obtained (Table 2).

Table 2 Results of Evaluation of S.C.T. by SVET



Measurement of the etching weight (FIG. 2) did not show a difference between the Zn-coated steel sheet and the Zn-4%Al-0.1%Mg alloy-coated steel sheet, but measurement of the Ni deposition weight (FIG. 3) made it clear that the Zn-4%Al-0.1%Mg alloy-coated steel sheet has a greater Ni deposition weight than the Zn-coated steel sheet, arguing that its reactivity is higher.



After applying a surface conditioning treatment under various conditions, we did a coating-type chromate treatment and prepared coated steel sheets, some with a 5-micron coating of epoxy resin type paint, and some with a 15-micron coating of polyester resin type paint. Using these coated steel sheets, we evaluated the paint film adhesion at 2t bends and the corrosion resistance in salt-water spray tests (720 hr) at 4t bends (FIG. 4, FIG. 5).

From FIG. 4 and FIG. 5 it is clear that the evaluation results of the paint film adhesion and the corrosion resistance to correspond to the evaluation of the treatability by SVET.



4. STATE OF SLUDGE PRODUCTION AT THE PILOT LINE

We applied the new acid-type surface conditioning treatment on the pilot line for Zn-coated steel sheet and Zn-4%AI-0.1%Mg alloy-coated steel sheet and investigated the state of sludge then produced in the treatment solution.

(1) We conducted experiments in which Zn-coated steel sheet was treated 185000 m² treatment, and we analyzed the Zn and Al concentration in the treatment solution at every time 1000 m² was treated (FIG. 6). After treated 60000 m² the Zn concentration in the treatment solution reached about 10000 mg/l. After that the fluctuation of Zn concentration becomes small. The replenishment amount of the treatment solution (fixed quantity replenishment), the amount of dissolved Zn elution into the treatment solution, and the amount of carried out treatment solution amount carried out by the treated Zn-coated steel sheet balanced, and it is presumed that the Zn concentration reached the balance point.

At this state Zn concentration of the treatment solution is not exceed the solubility of Zn (45000 mg/l), and therefore of course no sludge production was found.

The fluctuation of Al concentration was small, and Al concentration was approximately 3000 mg/l at most.

In conventional alkali-type surface conditioning treatment, the Zn solubility of the treatment solution is calculated to be 2500 mg/l. Therefore when the Zn concentration in the treatment solution reaches 2500 mg/l, sedimentation occurs in the form of Zn(OH)₂, and produce a sludge. The

values measured in tests reached 1900 mg/l in the initial stage and the Zn concentration value was constant and stable. It is presumed that the etched Zn almost precipitates out.

(2) The Zn-4%Al-01%Mg alloy-coated steel sheet was treated 1500 m² (FIG. 7). The Zn concentration in the treatment solution showed little fluctuation and was approximately 2000 mg/l at most. But the Al concentration in the treatment solution reached 10000 mg/l. At this time, 0.1 g/l of sludge was observed.

In conventional alkali-type surface conditioning treatment, sludge was produced by mainly $Zn(OH)_2$, but with the new acid-type treatment, sludge was produced by mainly SiO_2 . The SiO_2 sludge has greater fluidity than the $Zn(OH)_2$ sludge and has the advantage that was easily eliminated from the system by filtering or sediment removal.





REFERENCE

1. H. Fukumoto, H. Mizuki and K. Masuhara, Proceeding of GALVATECH '89 p. 577 (1989)

<u>Х-</u>б

QUESTIONS AND ANSWERS

	Why did you choose nickel and not cobalt for the metallic ion?
<u>Mashihara:</u>	We think Co is good in alkaline solution but Ni is better in acid.
Gerenrot:	If I understand, you have an ion exchange mechanism involved here, so Ni is reduced and coats Zn and Zn is dissolved and goes into solution. What is the nature of the sludge?
<u>Mashihara:</u>	It is mainly silicone oxide with some fluoric acid and aluminum.
Leroy:	I understand your system is acidic and that you are treating zinc, aluminum and magnesium and in your product you have a lot of Mg which is segregated at the surface is a non element, and you could etch your surface because you have a lot of Mg. This is not the case for everybody using Galfan because most producers do not have Mg in the alloy. I think the acidic pretreatment will not work if the Galfan alloy does not contain Mg. You must not say that this is a system for Galfan.
Hostetler:	This is an important point. I must take the responsibility for this contradiction because the paper submitted did specifically refer to Zn-4% Al-0.1 Mg.
Leroy:	Do the fluorides in your treatment require anything special for the tank material?
<u>Mashihara:</u>	The tank material is 316 alloy which is the same material used for the alkaline solution.

X-8

Report No.	WL/CP/P/1209/1/92/C
Date	13 August 1992
Classification	OPEN

PUBLISHED PAPER

Chrome-Free Systems for Galfan

to be Presented at the 17th Galfan Licensee Meeting in Tokyo, October 12th 1992

Welsh Laboratories Port Talbot West Glamorgan SA13 2NG Telephone: (0639) 871111 Telex: 48361 Telefax: (0639) 871111 Extn 2372



XI-2

13 August 1992 OPEN File No. 654

SUMMARY

CHROME-FREE SYSTEMS FOR GALFAN.

R.L. Quarshie, T. Mayes

Coated steel output has increased dramatically since 1970 with applications expanding in many markets. This has lead to an increasing number of new coated steels, one of which is Galfan. Galfan is being actively developed by ILZRO as the pre-paint substrate of the future. For Galfan to truly occupy such a market leadership role it must be compatible with any future developments related to coil coating.

At present there is a growing international awareness of the potential health problems associated with chromium, particularly the hexavalent variety. Hence, if Galfan is to be the material of the future it must be compatible with chrome- free systems.

This paper discusses the evaluation of various chrome-free pigments in primer systems on Galfan. This is part of a research programme sponsored by the European Coal and Steel Community, ECSC. The research involves the assessment of chrome-free primers made up of an epoxy base resin and various pigments. As, in the future, both chrome-free pretreatments and primers will be used by the coil coating industry, the total systems are examined. This involves the utilisation of a variety of chrome-free pretreatments. The initial results of physical, accelerated corrosion and natural weathering are discussed.

Overall, the tests undertaken show that chrome-free pretreatments and primers can work as efficiently as their chrome counterparts. However, they could not accurately determine the exact pigment system which would produce the best results. Hence, further investigation into these pigments is under way using electrochemical methods.

KEYWORDS

20

Galfan Chrome-free primers Chrome-free pretreatments Accelerated corrosion testing Natural Weathering Electrochemical Testing ECSC Project

British Steel Technical Welsh Laboratories Port Talbot, West Glamorgan SA13 2NG Telephone: (0639) 871111 Telex: 48361 Telefax: (0639) 872372

Cover Pages:	1
Text Pages:	11
Figure Pages:	6
Appendix Pages:	-

Initial Circulation

Strip Products

Dr. A.L. Vickers Mr. J. Mathieson Mr. A.E. Matthews Mr. J. Robinson

Shotton Works

Dr. I. Earnshaw Mr. R.G. Vyse

Tafarnaubach Works

Mr. J.A. Cronin

Bryngwyn Works

Mr. G.G. Stockden

ECSC

Dr. R. Salkin (2)

British Steel Technical

Dr. R. Baker

Swinden Laboratories

Dr. M.J. May Dr. D. Dulieu Mr. K. Johnson

Welsh Laboratories

Mr. E.F. Walker Dr. R.B. Smith Dr. K.G. Lewis Dr. T.J. Goodwin Mr. G.A. Jenkins Tech Doc (3 + 1*)

* Summary Only

The contents of this report are the exclusive property of British Steel plc and are confidential. The contents must not be disclosed to any other party without British Steel's previous written consent which (if given) is in any event conditional upon that party indemnifying British Steel against all costs, expenses and damages claims which might arise pursuant to such disclosure.

Care has been taken to ensure that the contents of this report are accurate, but British Steel and its subsidiary companies do not accept responsibility for errors or for information which is found to be misleading. Suggestions for or descriptions of the end use or application of products or methods of working are for information only and British Steel and subsidiaries accept no liability in respect thereof. Before using products supplied or manufactured by British Steel or its subsidiary companies the customer should satisfy himself of their suitability. If further assistance is required, British Steel within the operational limits of its research facilities may often be able to help.

COPYRIGHT AND DESIGN RIGHT - © - BRITISH STEEL, 1992
1. INTRODUCTION

Coated steel output has increased dramatically since 1970 with applications expanding in many markets. This has lead to an increasing number of new coated steels, one of which is Galfan. Galfan, with its 5% aluminium and 95% zinc coating, is claimed to have superior paintability, corrosion resistance and flexibility compared with a pure zinc coating⁽¹⁾. Hence, Galfan is being actively developed by ILZRO as the pre-paint substrate of the future. In order to meet this objective, Galfan must be compatible with both the pretreatment and painting systems of the future.

Currently chromates are used extensively in both pretreatment and primer systems, having a proven performance record for corrosion protection of steel. However, there is a growing international awareness of the potential health problems associated with chromate pigments, particularly the hexavalent variety.

Results of a number of independent investigations indicate that there is a potential health risk associated with the continued use of chromate pigments in the coatings industry⁽²⁻⁸⁾. Owing to this realisation and the measures being introduced to control their use^(9,10), paint companies have started to look for more environmentally favourable alternatives. Similar work is under investigation by the pretreatment manufacturers.

This paper discusses the evaluation of various chrome-free pigments in primer systems on Galfan. Thus the research involved the assessment of various chrome-free primers made up of an epoxy base resin and various anticorrosion pigments. As, in the future, both chrome-free pretreatments and primers will be used by the coil coating industry, the total systems were examined.

2 SUBSTRATE EVALUATION AND PANEL PREPARATION

2.1 Unpainted Galfan Substrate

0.7 mm 250 g/m² Galfan was used as the substrate for the chrome-free evaluation.

The specific surface morphology and composition of the Galfan material supplied was determined prior to application of the pretreatments and primers. This involved SEM examination and analysis of the Galfan coating. Both the top and bottom surfaces revealed similar morphology. Fig. 1 illustrates the general appearance of the surfaces. A slightly elongated grain structure was apparent. At higher magnifications, the grains showed fine lamellae and rod like eutectoid dendrites. Microanalysis of the Galfan surface showed it to contain 6% - 12% aluminium, in zinc. The chemical composition of the Galfan alloy is 4.25% aluminium and 0.26% iron.

Examination of the cross section through the Galfan coating revealed a continuous coating, 25 microns thick, having a primary dendritic phase and a fine lamella or rodlike eutectoid secondary phase Fig.2. Microanalysis of the primary dendritic phase (A) showed it to be predominately zinc, with only small amounts of Al (0.6-1.1%) and Fe (0.6-3%). Analysis of the eutectoid secondary phase (B), however, revealed 5.9% to 8.8% Al and 0.6% to 2% Fe in the zinc.

2.2. Painted Panel Preparation

2.2.1 Pretreatments

The effectiveness of two chrome-free pretreatments, A and B, were studied. In addition, one current chromate-based pretreatment, C, has been included as a control.

2.2.2 Pigments for Primer Formulation

Five different chrome-free pigment systems have been used in preparing in-house primers for the study. These are:

- (i) Pigment 1 an organosilicate mixture composed in-house,
- (ii) Pigment 2 a calcium/silica ion-exchange pigment,
- (iii) Pigment 3 an inorganic pigment based on barium metaborate
- (iv) Pigment 4 a zinc phosphate/zinc borate mixture
- (v) Pigment 5 a silica-based pigment
- 2.2.3 Primers and Topcoat

Epoxy polyester was chosen as the base resin for the primers. Proprietary chrome-free and standard chromate primers were selected as controls. PVF_2 was chosen as the topcoat. All the polymeric materials were supplied by a leading European paint company.

2.2.4 Paint Preparation

Each primer system was manufactured by adding the correct proportion, by weight, of the respective pigment to a pre-weighed base resin and mixing together. The pigment was then thoroughly dispersed using an Eiger 'mini' motormill (Type M-50-SSE) until a wet film thickness of 10 microns, determined using a Hegmann gauge, showed no readily discernable solid particles.

2.2.5 Panel Preparation

The chromate-based pretreatment, C, was applied to the Galfan by the conventional two stage immersion process. Both chrome-free pretreatments, A and B, were applied by a one stage dry-in-place process.

The primers and topcoat systems were bar coated using standard laboratory methods. The resultant dry film thicknesses were 9 and 25 microns for the primer and topcoat, respectively.

3. PANEL EVALUATION AND RESULTS

The primers were assessed under three main test regimes;

- (1) Physical Tests
- (2) Natural Weathering
- (3) Accelerated Corrosion Tests

3.1 Physical Tests

Poor adhesion of paints to metal substrates inevitably results in poor corrosion performance. The standard European Coil Coating Association (ECCA) test methods;

- (i) Reverse Impact Resistance,
- (ii) T-bend test and
- (iii) Crosshatch Erichsen dome method,

were used for testing paint adhesion to steel substrates, as well as inter-paint adhesion.

3.1.1 Reverse Impact Resistance (ECCA-T5(1985))

The maximum impact energy at which there is no visible crack in the coating, for fully finished panels, was determined for samples conditioned at room temperature (20°C). This resistance to cracking was observed at a x 20 magnification.

All of the primer systems passed the accepted level of 10J reverse impact.

3.1.2 T-bend Test (ECCA-T7 (1985))

All the primer-only and selected fully finished samples were tested for their flexibility by taking each sample through different substrate bend diameters (T-bends). The minimum bend diameter at which there is no visible crack in the coating was determined for each sample.

Figure 3 compares the T-bend test performance for all the systems. The performance of the primers over the pretreatment C (chromate-based) is highlighted. Apart from Pigment 3 and the standard chromate primers, all the other pigments are shown to marginally reduce the adhesiveness of the base resin. Similarly, the effect of pretreatment type on the adhesive properties of the epoxy base resin is shown. A different spread of primer adhesion performance is shown for each pretreatment. The careful choice of a primer system to match a particular pretreatment cannot be over-emphasised.

Figure 4 shows the relative performance of the standard chromate and chrome-free primers over each pretreatment on Galfan. The better performance of the chrome-free primer over the chrome-free pretreatments is evident.

3.1.3 Cross-hatch Erichsen Dome Method (ECCA-T6 (1985))

The standard cross hatched Erichsen dome method was applied to all the primer-only and selected fully finished panels. The samples were subjected to 7-8 mm Erichsen draw. Sellotape was used to remove each coating, under an average human-force. The percentage loss of adhesion was determined by the amount of paint removed by the tape. All the primer/pretreatment systems under study performed satisfactorily in all the tests with 100% adhesion.

Overall, very good mechanical properties are shown for all the primer/pretreatment systems.

3.2 Natural Weathering

Natural weathering is the effect of outdoor exposure on a material's properties and service performance. In the case of coatings, the weather can cause changes through a number of chemical and physical reactions due to dimensional changes in substrate, swelling by water and fluctuations in temperature. Volatilisation of solvents, leaching of pigments, chemical decomposition of main polymer chains in a coating vehicle (i.e. binder) and stressing and deformation of a coating can occur. The main weathering factors causing change include, sunlight, oxygen and ozone, humidity, precipitation and atmospheric contaminants. All these factors contribute individually, and in combination, to change the properties of coatings through the reactions just mentioned. The degree of change depends on the intensity of these factors in a particular weathering environment.

Three different locations in the UK, representing typical Northern European environments, were selected as the weathering sites.

- (a) Rye located in East Sussex and is described as severe marine.
- (b) Cockett situated close to Swansea in South Wales; it is described as urban coastal.
- (c) Research Centre located at the British Steel Welsh Laboratories, Port Talbot. The environment is described as mild industrial.

Figure 5 shows the location of each site on a map of the UK. Most of the samples prepared for exposure were coated with PVF_2 . However, some selected primer-only systems were included. Each of the samples prepared had four cut edges, one simulated building profile, one punch hole (for a labelling tag) and one fastener. Figure 6 shows a picture of a typical test panel.

The painted Galfan samples have been on exposure since December 1990. Table 1 shows the performance of the samples exposed at the Rye weathering site, after 12 months exposure. Of the three sites, Rye is the

most aggressive and therefore gives a good indication of the comparative performance of the coatings. The results show that apart from some slight degradation at the cut-edges, no significant change had occurred across the painted surface. Pigments 4 and 5 show the best performance on all three pretreatments. Pigment 3 is shown to be performing well on pretreatment C but not as well on the two chrome-free pretreatments. Conversely, the standard chrome-free primer is shown to be performing better on the two chrome-free pretreatments.

3.3 Accelerated Corrosion Tests (ECCA Tests)

Accelerated corrosion tests have as their primary objective the prediction, or estimation, of long-term environmental effects by the use of short-term tests. For these short-term tests, the factors that comprise weathering environments are simulated in a laboratory but at an exaggerated level, in order to accelerate the degradation reactions mentioned earlier.

The following accelerated corrosion test methods were employed:

- (a) Salt Spray
- (b) Water Soak
- (c) Humidity
- (d) Kesternich SO_2
- (e) Prohesion

The samples for the accelerated corrosion tests were all prepared to simulate panels with building profiles, scribe indents and cut edges. Both primer-only and fully finished panels were prepared for testing.

Tables 2 and 3 show typical observations for all of the tests performed, at the scribes. The results are selected to reflect the typical performance of the primers on a chrome-free pretreatment as compared to the chrome pretreatment.

3.3.1 Performance in Salt Spray (ECCA-T8(1985))

In general, the samples gave good results. There were no obvious differences between the pretreatments or pigments. This is probably due to the severity of the test.

3.3.2 Performance in Water Soak (ECCA-T9(1985))

Both the chrome-free pretreatment A and chrome pretreatment C gave very good results, with only slight staining at the scribe for all of the paint systems tested. However, panels pretreated with pretreatment B exhibited both staining at the scribe and blistering over the surface in general.

3.3.3 Performance in Humidity (BS3900 Part F2)

Again the results for all of the systems were similar. However, the chromate pretreatment did give slightly improved performance.

3.3.4 Performance in Kesternich SO₂ (ECCA-T16 (1985); DIN50018)

Both the chrome-free pretreatment A and chrome system C gave similar results. However, the other pretreatment gave poor results with under cutting and flaking at the cut edge and scribe for all of the paint systems. In the most severe cases, primers containing pigments 4 and 5 and the standard chrome-free primer resulted in a complete loss of adhesion at the scribe.

3.3.5 Performance in Prohesion⁽¹¹⁾

Fresh PVF_2 painted samples were subjected to 1000 hours of cyclic wetting and drying. An aggressive mist made up of ammonium sulphate (3.5 g/l) and sodium chloride (0.5 g/l) was used in the wet cycle at

ambient temperature. During the dry cycle, the samples were air-dried, using forced-air circulation, at 35°C. Sample observations were made every 250 hours.

Figure 7 shows the degree of creep present at the scribe after testing. These results indicate that the performance of the primer system does not vary considerably. Again the performance of all of the systems was good.

4. CONCLUSIONS

The following conclusions can be drawn from the work undertaken:-

- (i) There is good cohesion within the chrome-free primers.
- ii) There is satisfactory adhesion between:
 - (a) chrome-free primers/chrome pretreatments,
 - (b) chrome-free primers/chrome-free pretreatments,
 - (c) chromate primers/chrome-free pretreatments.

For optimum performance the chrome-free primer must be carefully chosen to match the choice of chrome-free pretreatment.

- (iii) One year outdoor exposure at a severe marine environment has identified no significant problem with painting Galfan with chrome-free pretreatments and primers.
- (iv) Accelerated corrosion tests have shown no significant reduction in performance of the complete chrome-free systems compared to the chrome-containing systems

Overall, the tests undertaken show that chrome-free pretreatments and primers can work as efficiently as their chrome counterparts. These tests, however, could not accurately determine the exact pigment system which would produce the best results. Hence, further investigation into these pigments is under way using electrochemical methods.

5. ACKNOWLEDGEMENTS

The authors wish to thank Dr. R. Baker, Director of Research and Development, British Steel Technical, and Mr. E.F. Walker, Manager, Welsh Laboratories and Strip Mill Products, British Steel Technical for permission to publish this paper. The authors wish to thank the European Coal and Steel Commission (ECSC) for giving permission to use the results in this paper and their support for this work.

6. **REFERENCES**

- 1. Roman and Lynch, "Galfan: A World Overview",(1990)
- 2. Langard and Norseth, Brit. J. Ind. Med., 32(1975) p82
- 3. Langard and Vigander, Brit. J. Ind. Med., 40(1983) p71
- 4. Davies, JOCCA, 62(1979) p157 and Brit. J. Ind. Med., 41(1984)p158;170
- 5. Sheffect et al., Arch. Environ. Health, 37(1982)p44
- Davies, J.M., "Lung Cancer Mortality of Workers making Chrome Pigments", Lancet, 1(1978)p384
- 7. Dolager et al., J. Occup. Med., 22(1980)p25
- 8. Levy et al., Brit. J. Ind. Med., 43(1986)p243

- 9. U.S. Environmental Protection Agency, "Health Assessment Document for Chromium", Final Report, EPA-600/8-83-014F (1984)
- 10. UK Health and Safety Executive document on chromium, in preparation
- 11. British Steel Technical, Welsh Laboratories quality system operating procedure, reference CP/08/05, (1992)

R.L. Quarshie Senior Research Officer

T. Mayes Research Officer

Dr. T.J. Goodwin Manager Coated Products Technology

RLQ/TM/2033

•

.

TABLE 1 EXTERNAL WEATHERING OF PVF2-PAINTED GALFAN IN A SEVERE MARINE ENVIL

Site: Rye.

Exposure Period: December 1990 - December 1991

Edge Condition.

		Pretreatment	
Sample (with PVF ₂ topcoat)	A (Chrome-free)	B (Chrome-free)	C ((
Standard chromate	Flaking <1mm	M < 8, 1mm	M
Standard Chrome-free	F<8, <1mm	F8, 1mm	M6&
Unpigmented	M8, 1mm	M6&8, 1-2mm & Slt flaking	
Pigment 1	M<8, 1mm & very Slt flaking	M6&8, 1-2mm & Slt flaking	М
Pigment 2	M<8, 2mm & very Slt flaking	M8, 1mm	
Pigment 3	M<8, 2mm & very Slt flaking	MD8, 1-2mm	[
Pigment 4	F<8, 1mm	F8, 1mm	
Pigment 5	F<8, 1mm	F8, 1mm	

KEY: F = Few, M = Medium, MD = Medium Dense, D = Dense, VF = Very Few, Slt = Slight

Comment

In all cases there was no chalking of the PVF_2 and the colour was retained. The profiles and panels in general were

XI-12

<u>TABLE 2</u> <u>ACCELERATED CORROSION TESTING OF PVF2 TOPCOATED CHROME-FREE PRIMERS</u>

Pretreatment C Sample Condition: Test Duration:	at Scribes 1000 Hours for salt s	pray, Prohesion, w	ater soak and humidity tests, 20 c	ycles for Kesternick
Sample			Test Method	
Gample	Salt Spray	Prohesion	Water Soak	Kesternich
Standard Chromate	F-M 6&8, 2mm Trace W/R	Pristine	Slt Staining < 3mm	D8, 1-2mm Slt I
Standard Chrome-free	F8, 1mm Trace W/R	D8, 1mm	Slt staining < 2mm	D8, 2mm Slt R
Unpigmented	D4&6, 2-4mm Mod W/R	D8, 1-2mm	M-MD < 8, 1mm Slt staining	D8, 1-2mm Sit 1
Pigment 1	D2,4&6, <12mm Mod W/R	MD < 81mm	D6&8, 1-3mm Trace W/R	D6&8, 2mm Slt
Pigment 2	D2, 4,6&8 <12mm	D6 &8, 2mm	D6&8, 2-3mm Trace W/R	D6, 2mm Slt R
Pigment 3	D2,4,6& 8 < 12mm Mod W/R	D6&8, 2-4mm	D6&8, 2-3mm Slt W/R	D6, 2-3mm Slt F
Pigment 4	D2,4&6 < 12mm	D6&8, 2mm	D6&8, 2-3mm Trace W/R	D6, 2mm Slt R
Pigment 5	D2,4&6 2-8mm Mod W/R	D6&8, 2mm	D6&8, 1-3mm	D6, 2mm Slt R

KEY: F = Few, M = Medium, MD = Medium Dense, D = Dense, Mod = Moderate, R/R = Red Rust, W/R = White Moderate R/R = Red Rust, W/R = White Rust, W/R = White Moderate R/R = Red Rust, W/R = White Ru

TABLE 3 ACCELERATED CORROSION TESTING OF PVF1 TOPCOATED CHROME-FREE PRIMERS

Pretreatment A Sample Condition at So Test Duration:	cribes 1000 Hours for salt spi	ray. Prohesion, water s	soak and humidity tests 20 cv	cles for Kesternich SO ₂
			Test Method	
Sample	Salt Spray	Prohesion	Water Soak	Kesternich
Standard Chromate	MD6,8& <8 , 1-4mm M W/R striating	F<8, 1mm	Slt staining 1-2mm	U/C 2-4mm Trace
Standard Chrome-free	MD4,6&8, 1-4mm Slt W/R striating	D8& <8, 1-2mm Slt W/R	F-M<8, 1mm Slt striating	D6&8,1-3mm Trace
Unpigmented	D2, 4&6, 5-15mm D W/R striating	D6& <8, 1-4mm Mod W/R	F-M <8, 1-3mm Slt staining & striating	U/C & F2, 1-3mm Sl
Pigment 1	D2, 4&6, 4-12mm D W/R striating	MD8 & <8, 1-2mm Trace W/R	Slt staining	U/C 2-3mm
Pigment 2	D4, 6&8, 1-10mm Mod W/R	MD8 & <8, 1-2mm Mod W/R	VF <8, 1mm Slt staining	U/C 2-4mm Trace
Pigment 3	D2, 4&6, 5-15mm D W/R striating	MD8& <8, 1-2mm Mod W/R	F-M<8, 1mm Slt-Mod staining	U/C 1-3mm Slt R
Pigment 4	D2,4,6& 8, 2-10mm D W/R striating	MD8&<8, 1-2mm Trace W/R	F-M <8, 1mm Slt staining	U/C 2-4mm Trace
Pigment 5	D2, 4&6, 2-12mm D W/R striating	D6&8, 2-3mm Mod W/R	MD<8, 1mm Slt staining	U/C 2-4mm Trace R/R & F
		f		1

KEY:- F = Few, M = Medium, MD = Medium Dense, D = Dense, Mod = Moderate, R/R = Red Rust, W/R = White Ru



FIG.2



SURFACE MORPHOLOGY OF GALFAN.

FIG.1







T-BEND FLEXIBILITY FOR PIGMENTED PRIMERS FIG. 3



(TM/CP/F4) COMPARISON OF THE ADHESION PERFORMANCES OF THE STANDARD FIG. 4 CHROMATE AND CHROME-FREE PRIMERS OVER BOTH CHROMATE-BASED AND CHROME-FREE PRETREATMENTS ON GALFAN



(TM/CP/F5/J1) A SECTIONED MAP OF THE U.K. SHOWING LOCATION AND FIG. 5 CLASSIFICATION OF THE WEATHERING SITES



(TM/CP/F6) AN EXAMPLE OF A TYPICAL SAMPLE DESIGN FOR NATURAL FIG. 6 WEATHERING TRIALS



(TM/CP/F7) DEGREE OF CREEP AT SCRIBE AFTER 1000h PROHESION FIG. 7 XI-20

SECTION XI APPENDIX

QUESTIONS AND ANSWERS

Yesterday our colleague from CRM made us aware that the presence of magnesium in the Capul: GALFAN was very important when discussing pre-treatments. Can you tell us whether the GALFAN tested here contained Mg? The GALFAN composition is not described. Stoneman: I think it is safe to assume the GALFAN sheet has European sources which would mean Chairman: no Mg was added. Can you tell me what was the composition of the passivation film? There are no details in the paper. Stoneman: Were the samples painted in the laboratory or on an industrial paint line? Dubois: They were bar coated (in the laboratory). Stoneman: I am interested in the cost of the non-chrome passivation system. No, there is no discussion in the paper about cost. I am sure we can obtain that Stoneman: information from British Steel. We admittedly asked British Steel to make this progress report before they were Chairman: anticipating to do so. I am sure this, and many of the other questions, will be answered in future progress reports. After Galvatech 92, I visited Henkel Technimetal GmbH and met with Dr. Roland. He Taiiri: said the purpose of chrome-free is prevention of pollution of waste water or sludge and to prevent pollution by long-term exposure. Do you agree with this opinion?

Section XI-Appendix (cont'd.)

Stoneman:	Personally, yes. The reason in the paper is to find an acceptable substitute for hexavalent chrome solutions which will be expensive or impossible to dispose of under impending legislation.
<u>Williams:</u>	This problem of chrome-containing treatments has become of such proportion for a company like British Steel that we must apply to regulatory councils for licenses to use such solutions and prove that certain precautions are used to protect nearby (a) workers and (b) the environment. Additionally, the air containing the fumes and the water containing the solutions must wash or filter the chromes out before discharging the waste from the plant. We are even required to provide personnel monitors at times to make certain exposure levels of chrome in the atmosphere do no exceed specified levels. We have had to make large expenditures to redesign the process equipment to reduce the handling of the chrome bearing solution by workers. It has forced us to change from handling barrels and drums to the use of bulk storage tanks and automatic solution control.
<u>Tajiri:</u>	Dr. Roland says rolled on chromate is better than sprayed chromate treatment because roller type is dried-in-place. He says chrome-free coating is difficult.
<u>Williams:</u>	Yes. I agree. We have run line trials with chrome-free systems from Oakite and Chemcoat on hot dip coatings. We are still evaluating those trials and as you say, cost is important.
Gerenrot:	What is the suspension media for the pigment?
Stoneman:	Epoxy polyester.
Gerenrot:	What are the layer thicknesses?
Stoneman:	The primer is 9µm; the top coat is 25µm.
Gerenrot:	What thickness for the pre-treatment?
Stoneman:	10 microns.
Gerenrot:	Is there no chemical reaction between the GALFAN surface and the pre-treatment such as with a chromate pre-treatment? Is the cohesion only mechanical?
Stoneman:	I think you are correct. That would follow from what was presented.

Darkening of Galfan and packing (The effctiveness of various packing in preventing the darkening of Galfan steel sheets)

ISAO NAGANO

YODOGAWA STEEL WORKS, LTD.

1. Introduction

When coil and seet products manufatured from Galfan steel sheets are stored by users for a long period, the products age and the surfaces become discolored and darkened. Galvanized steel sheets also are affected by moisture condensation and convered with white rust. The atempts to prevent these defects have generally involved chemical treatment.

We have investigated the effect of volatile corrosion inhibitor (VCI)paper as packing (wrapping) paper for galvanized products. The VCI paper contains volatile, durable corrosion inhibiting chemicals. Therefore, the following features are available.

- The corrosion inhibitor volatilizes immediately after the packing material is used and quicklip the reaches the effective gas concentration. This develops an initial rust-preventive effect.
- Volatilized corrosion inhibitor gas permeates every area in packing.
- The durable component of the corrosion inhibitor retains its corrosion inhibitory effect over a long period of time.

 If moisture is contained in packing or moisture permeated from the outside condenses, the effective component of VCI paper is dissolved and prevents rust from forming.

We have tested whether these features are effective for preventing the darkening of Galfan steel sheets and the growth of white rust on galvanized steel sheets. The test results are reported below.

2. Kinds of packing paper tested

No	Packing paper	Specifications
1	Moisture-proof paper	Laminated paper.
2	Moisture-proof paper	Sandwiched PP film.
3	VCI Paper	Extrusion laminated polyethylene mainly composed of carboxylates produced by I company.
4	VC1 Paper	Extrusion laminated polyethylene mainly composed of carboxylates produced by K company.
5	Corrosion inhibitor paper ① for surface-treated steel sheet.	Laminated products mainly commposed of amine der ivatives of carboxylates developed for Zn-Ni.
6	Corrosion inhibitor paper ② for surface-treated steel sheet.	Laminated products mainly commposed of amine der ivatives of carboxylates developed for Zn-Ni.

3. Steel sheets tested

a	Galfan steel sheets	0.80mm	Y25	RS	non-treated
ь	Galvanized steel sheets	0.50mm	Z25	ZS	non-treated

4. Test method

temperature-humidity cycletest :

1)Apparatus : Constant-temperature, constant-humidity bath.

2)Cycle condition :

① Temperature 0 °C, humidity OFF, for 3 hours

2 Temperature 50 °C, humidity 95%, for 3 hours

③ Temperature 0 ℃, humidity OFF, for 2 hours

④ Temperature 50 ℃, humidity 95%, for 16hours

Applying the above for steps as one cysle, each galvanized steel sheets specimen was subject to tests for the number of cycles indicated in Table 1.

3)Test spesimen treatment and packing method :

Each steel sheet was cut into 60×80 mm specimens. The specimens were cleaned with hot toluene, hot acetone, and water, then dried. A stack of five specimens was wrapped with various kinds of packing paper(size 110×180 mm)as shown in Figure 1, then subject to the temperaturehumidity cycle tests.

The table in item 5, test results, shows the measured surface number (n) of five stacked specimens. Note that an odd number n indicates the top and an even number of n the rear of a steel sheet, respectively.

《Figure.1》







4) The number of cycle and the criteria for the tests

	Test steel sheet	Number of cycles	Presence or absence of spacer and number of n	Criteria				
i		-		*Criterion : Resistance to darkening				
				$(Weak) \otimes > \bigcirc > \bigcirc > \bigcirc > \land > \times (Strong)$				
				$\odot: No discolration$				
		N 1	December and sharman	○:Low degree of darkening				
а	Galfan Number of Pre steel sheet cycle 10 n =	n = 2	: Middle degree of darkening in partial area					
				△:High degree of darkening in partial area				
			× :High degree of darkening in whole area					
				*:Corrosion in partial area				
				(See the attached Photo 2)				
				*Criterion :Presence to the growth of white rust				
				(Thin) ◎>○>△>× (dense)				
				◎:No white rust				
b	Galvanized steel sheet	Number of cycle 20	Presence and absence $n = 2$	○:Low degre of white rust in partial area				
				△:Middle degree of white rust in partial area				
				× :High degree of white rust in partial area				
				(See the attached Photo 3)				

《Table 1》

5...Test results

a. Galfan steel sheets (tested for 10 cycle using the degree of the darkening as the

criteria)

	j	10	6			Ē			6	0	(10)
lest sample/Measured surface	n 	U	2	3	4	9	Ø		8	. 9	
Without spacers				·		,	· ·····	.	·····		
<pre>①Moisture-proof paper (Laminated paper)</pre>	1 2	× ×	× ×	××	× ×	× ×	× ×	× ×	× ×	× ×	× ×
②Moisture-proof paper (Sandwiched PP film).	1 2	× ×	× ×	× ×	× ×	× ×	× ×	× ×	××	× ×	× ×
③VCI Paper (by comany I)	1 2	× ×	\triangle	\triangle	$\stackrel{\triangle}{\times}$	$\stackrel{\triangle}{\scriptstyle \Delta}$	$\stackrel{\triangle}{\scriptstyle \Delta}$	$\stackrel{\triangle}{\scriptstyle \triangle}$	$\stackrel{\triangle}{\scriptstyle \triangle}$	$\stackrel{\triangle}{\scriptstyle \bigtriangleup}$	× ×
<pre>④VC1 Paper ((by comany K)</pre>	1 2	× Δ	$\stackrel{\times}{\Delta}$	× ×	× ×	× ×	$\stackrel{\triangle}{\times}$	× ×	$\stackrel{\bigtriangleup}{\times}$	$\stackrel{\times}{\bigtriangleup}$	× ×
SCorrosion inhibitor paper	1	0*	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	0*
steel sheet.	2	0*	Δ	Δ		Δ	Δ	Δ	Δ	Δ	0*
©Corrosion inhibitor paper	1	0*	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	0*
② for surface-treated steel sheet.	2	0*	Δ	Δ		Δ	Δ	Δ	Δ	Δ	0*
·	·	·	·	·	·	·	·	, <u> </u>	· ·	·	· 1
Test sample/Measured surface	<u>n</u>	1	2	3	4	5	6		8	9	0
With spacers											
<pre>①Moisture-proof paper (Laminated paper)</pre>	1 2	× ×	× ×	× Δ	× ×	× ×	× ×	× ×	× ×	× ×	× ×
②Moisture-proof paper (Sandwiched PP film)	1 2	× ×	× ×	× ×	× ×	× ×	× ×	× ×	× ×	× ×	× ×
③VCI Paper (by comany I)	1 2	× ×	× △	\triangle	$\stackrel{\triangle}{\times}$	$\stackrel{\triangle}{\scriptstyle \triangle}$	$\stackrel{\triangle}{\frown}$	$\stackrel{\triangle}{\scriptstyle \triangle}$	$\stackrel{\triangle}{\vartriangle}$	$\stackrel{\Delta}{\scriptstyle\Delta}$	× ×
<pre>④VCI Paper ((by comany K)</pre>	1 2	× ×	× △	× ×	$\stackrel{\times}{\bigtriangleup}$	× △	× Δ	× ×	× ×	× △	× ×
©Corrosion inhibitor paper	1	0		Δ	Δ	Δ	Δ	Δ	Δ	Δ	0*
steel sheet.	2	0	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ	0*
©Corrosion inhibitor paper	1	0	Δ	Δ	Δ	Δ	Δ	0	0	0	0*
CONTRACTOR SUCCESSION	((ł	1	()	[(()	

Criterion : Resistance to darkening

(Weak) $\bigcirc > \bigcirc > \bigcirc > \bigcirc > \land > \times$ (Strong)

(See the attached Table. 1 and Photo 2)

b. Galvanized steel sheets (tested for 20 cycle using the degree of white rust

formation as the criterion)

Test sample/Measured surface	n	1	2	3	4	(5)	6	T	8	(9)	10
Without spacers											
①Moisture-proof paper (Laminated paper)	1 2	© △	00	00	00	00	00	00	00	00	$\stackrel{\triangle}{\bigtriangleup}$
②Moisture-proof paper (Sandwiched PP film)	1 2	0 0	00	00	00	00	00	00	00	00	∆ 0
③VCI Paper (by comany I)	1 2	00	00	00	00	00	© 0	© 0	© 0	00	00
<pre>④VC1 Paper ((by comany K)</pre>	1 2	00	0 0	0 4	00	00	00	00	0 0	0	00
©Corrosion inhibitor paper	1	×	×	×	Δ	Δ	Δ	Δ	×	×	×
steel sheet.	2	×	×	×	Δ	Δ	×	×	×	×	×
© Corrosion inhibitor paper	1	×	Δ	Δ	Δ	Δ	Δ	Δ	×	×	×
steel sheet.	2	×		\bigtriangleup	\triangle	\triangle	\bigtriangleup	Δ	×	×	×
l	ł	Å	·								
Test sample/Measured surface	 	1	2	3	4	5	6	1	8	9	10
Test sample/Measured surface With spacers		0	2	3	4	5	6	Ī	8	9	10
Test sample/Measured surface With spacers ①Moisture-proof paper (Laminated paper)	n 1 2	① ◎ ○	2	③ △ △	 ④ △ ○ 	5 0 ©	€ △ ○		8 0 0	(9) △ ○	
Test sample/Measured surface With spacers ①Moisture-proof paper (Laminated paper) ②Moisture-proof paper (Sandwiched PP film)	n 1 2 1 2	① ◎ ○ ○ ○				 ⑤ ○ ○<	€ 0 00		⑧ ○ ○ △	(9)△○○○○	
Test sample/Measured surface With spacers ()Moisture-proof paper (Laminated paper) (2Moisture-proof paper (Sandwiched PP film) (3)VC1 Paper (by comany I)	n 1 2 1 2 1 2	 ① ○ ○	②○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○<	③ △ △ ○ ○ ○		© 00 00 00	⁽⁶⁾ ⁽²⁾	⑦○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○<	 ⑧ ○ ○<	●△○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○	
Test sample/Measured surface With spacers ()Moisture-proof paper (Laminated paper) ()Moisture-proof paper (Sandwiched PP film) ()VCI Paper (by comany I) ()VCI Paper ((by comany K))	n 1 2 1 2 1 2	⊕⊕0000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000000<				© 0 0 0 0 0 0 0 0 0	€△○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○<		⑧○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○<		
Test sample/Measured surface With spacers (Moisture-proof paper (Laminated paper) (Sandwiched PP film) (Surdwiched PP film) (VCI Paper (by comany I) (VCI Paper (by comany K) (Scorrosion inhibitor paper	n 1 2 1 2 1 2 1 2 1 2	① ◎ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○		③			€4000000000	(7) (10) <	 ⑧ ○○ ○	(9)△○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○	(1)
Test sample/Measured surface With spacers ()Moisture-proof paper (Laminated paper) (2)Moisture-proof paper (Sandwiched PP film) (3)VC1 Paper (by comany I) (4)VC1 Paper ((by comany K)) (5)Corrosion inhibitor paper () for surface-treated steel sheet.	n 1 2 1 2 1 2 1 2 1 2 1 2			③			€△○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○<		 ⑧ ○ ○		(1)
Test sample/Measured surface With spacers ()Moisture-proof paper (Laminated paper) (2)Moisture-proof paper (Sandwiched PP film) (3)VCl Paper (by comany I) (4)VCl Paper ((by comany K)) (5)Corrosion inhibitor paper (1) for surface-treated steel sheet. (6)Corrosion inhibitor paper (2) for surface-treated	n 1 2 1 2 1 2 1 2 1 2 1 2 1 2 1 2 1 2			③	 (4) (4) (5) (6) (7) (7)		€ 	⑦ ○ △ △ ○ △ ○ <t< th=""><th></th><th></th><th> ⓐ △ △ △ △ ○ ○</th></t<>			 ⓐ △ △ △ △ ○ ○

Criterion :Presence to the formation of white rust

(Thin) $\bigcirc > \bigcirc > \triangle > \times$ (dense)

[See the attached Table. 1 and Photo 3]

- a. Galfan steel sheets
- Both kinds of moisture-proof papers cause a high degree of darkening in the whole area.
- VCI paper by company I tends prevent darkening in the gas phase, but it causes a high degree of darkening in the area where the paper contacts the steel sheet.
- VCI paper by company K dose not prevent darkening.
- Corrosion-inhibitor papers ① and ② for surface-treated steel sheets prevent darkening effectively, but they cause corrosion in the area where the paper contacts the steel sheet.
- b. Galvanised steel sheets
- Both kinds of moisture-proof papers allow a relatively low degree of white rust.
- VCI paper by company I prevents the growth of white rust.
- VCI paper by company K prevents the growth of white rust.
- Corrosion-inhibitor papers ① and ② for surface-treated steel sheets are not effective in preventing the formation of white rust.
- 6. Conclusion
- a. For Galfan steel sheets, corrosion-inhibitor paper is effective in preventing Corrosion-inhibitorpapers ① and ② for surface-treated steel sheets are particularly effective.

Effective gas composed of volatilized chemicals, major components being amine derivatives of carboxylates, seems to protect Zn-Al alloy galvanized surface layers effectively. Corrosion occurs however, in the area where the paper contects a steel sheet. The probable reason is that, although volatilized gas is effective in preventing darkening, on direct contact the chemical apparently reacts with the surface layer of Zn-Al alloy galvanized steel sheet.

To store Galfan steel sheets for a long period of time, the effect of preventing darkening can be obtained wrapping with corrosion-inhibitor papers (1) and (2) for surface-treated steel sheets. It is, however, necessary to eliminate the factor that corrodes the paper-steel contact area. b. Although corrosion-inhibitor papers ① and ② for surface-treated steel sheets were effective for Galfan steel sheets, they are not effective in preventing the formation of white rust on galvanized steel sheets. A remarkable degree of white rust in observed.

Although there is on great difference between moisture-proof paper and corrosioninhibitor paper, corrosion-inhibitor papaers of both I and K companies are more effective.

Effective gas volatilized from chemicas, whose major component is amine derivatives of carboxylates, is ineffective for a Zn-galvanized surface; on the other hand, effective gas volatilized from chemicas, whose major component is single carboxylates, is effective. In short, corrosion-inhibitor paper consisting mainly of carboxylates is effective for storing galvanized steel sheets for a long period of time.

/End

Packing paper plan/Without spacers

Untie packing paper



(Hhoto 2) Galfan steel sheets(tested for 10 cycle using the degree of the darkening as the criteria)

◎ : No discolration



: Middle degree of darkening in partial area



× :High degree of darkening in whole area



○ : Low degree of darkening





* : Corrosion in partial area



《Hhoto 3》 Galvanized steel sheets (tested for 10 cycle using the degree of white rust formation as the criterion)



The residual mischmetal dross problem in a dual-purpose galvanizing line

Naotaka Ueda*, Mutsuo Sagara*, and Toru Takayama*2

Synopsis: Sumitomo has produced GALFAN with 0.1wt% mischmetal at the Wakayama Steel Works since 1987. Since a single fixed main pot for galvanizing is used in Wakayama Steel Works, the GALFAN bath is exchanged with the regular galvanizing bath. A mischmetal dross residue remained in the main pot after the removal of the GALFAN bath. Consequently, surface defects due to the granular-shaped dross composed of Zn-Ce or Zn-La intermetallic compounds appeared on regular galvanized steels. The solubility of mischmetal in the GALFAN bath is 0.01wt% at 450 °C and excess mischmetal is accumulated as a bottom dross composed of Zn-Ce or Zn-La intermetallic compounds. These compounds are lighter than the regular galvanizing bath. Therefore, the Zn-Ce or Zn-La intermetallic compounds become top dross in the galvanizing bath and cause surface defects. Sumitomo has solved this problem using the following three methods: (1) A decrease of mischmetal in the GALFAN bath, (2) The removal of GALFAN bottom dross, (3) Scraping with a stabilizing and a correcting roll.

1. Introduction

Sumitomo has produced GALFAN and regular galvanized steel (0.01wt%Pb) at Wakayama No.2 galvanizing line since 1987. Since the No.2 galvanizing line has a single fixed main pot. GALFAN and the regular galvanizing bath are exchanged with each other.

In producing galvanized steel, a granular-shaped dross defect appeared. The granularshaped dross defect is not appropriate for prepainted applications. Therefore, in this paper, the mechanism of the dross formation and the preventive methods are discussed.

2. Granular-shaped dross defect on regular galvanized steel

A granular-shaped dross defect has appeared on galvanized steel and none of GALFAN. However, Sumitomo has never experienced a granular-shaped dross defect on galvanized steel in the other galvanizing lines (Wakayama No.1 and No.3 galvanizing lines). Therefore, a granular -shaped dross defect is a specific problem at Wakayama No.2 galvanizing line which produces GALFAN and galvanized steel in a single fixed main pot.

Photo.1 shows the surface appearance of a granular-shaped dross defect on galvanized steel. The diameter of the dross defect is about 2 mm.

Photo.2 shows a cross section SEM micrograph of the dross defect. A compound with a diameter of about 70 μ m exists at the center of the dross defect. EDXA analysis shows the compound to be composed of Zn, Ce and La.

Thus, a granular-shaped dross defect is caused of Zn, Ce and La intermetallic compounds. Ce and La are intentionally only added in the GALFAN bath.

^{*} Wakayama Steel Works, Sumitomo Metal Industries, LTD. 1850 Minato, Wakayama City, Japan

^{*2} Iron & Steel Research Laboratories, Sumitomo Metal Industries, LTD. 660, Amagasaki City, Japan

3. Investigations of Ce and La in the main pot

GALFAN and galvanized steel are produced at Wakayama No.2 galvanizing line. GALFAN is produced for 5 days in a row once a month. Since the No.2 galvanizing line has a single fixed main pot, there are two storage pots, one for the GALFAN bath, and the other for the regular galvanizing bath. The GALFAN bath in the main pot is exchanged with the regular galvanizing bath through pipes linked to the storage pots (Figure 1).

Mischmetal is only added in the GALFAN bath for the purpose of preventing bare spots on the surface of GALFAN steel sheets. Sumitomo has used 0.1% mischmetal added GALFAN ingots. Table 1 shows the composition of the mischmetal. The main components of the mischemetal are Ce (50wt%) and La (30wt%). Table 2 shows the concentration of Ce and La in the main pot. The concentration of Ce and La under static bath condition is 0.003 wt% and 0.002 wt% at the top of the GALFAN bath, which is much less than that of the GALFAN ingot. The faster the line speed is, the higher the concentration is. Moreover, a viscous dross accumulated at the bottom, and the dross included 2.902 wt% Ce and 1.086 wt% La. When regular galvanized steel was produced for 5 hours after exchanging the bath, the concentration of Ce and La was 0.028wt% and 0.013wt% at the top of the galvanizing bath.

The concentrations of Ce and La at the top of the GALFAN bath were slightly lower than at 1m below the top at the static state, at the line speed of 36 m/min and 100 m/min. However, their concentrations in the regular galvanizing bath after exchange were high at the top of the bath than at 1m below the surface at the line speed of 100 m/min.

Figure 2 shows the rates of decrease in the concentrations of Ce and La in the bath after the bath exchange over a period of time. Also the viscous bottom dross in the hollow portion of the main pot decreases gradually in a regular galvanizing bath.

Photo.3 shows micrographs of a GALFAN bath (in a static state and during production). GALFAN bottom dross, and galvanizing bath which correspond to table 2. Zn, Ce and La intermetallic compounds are found in each micrograph. However, the sizes of the compound are different, that is, the GALFAN bath under static state has a small Zn. Ce and La intermetallic compounds ($\sim 30 \,\mu$ m) (Photo. 3A). During production, the size is $\sim 50 \,\mu$ m (Photo. 3B). The size of a GALFAN bottom dross is $\sim 200 \,\mu$ m (Photo. 3C). Moreover, the size of the compound in regular galvanizing bath is $\sim 200 \,\mu$ m (Photo. 3D). Therefore, in regular galvanizing bath, Zn, Ce and La intermetallic compounds are larger than in a GALFAN bath and are as large as those in GALFAN bottom dross.

4. Investigations Ce and La in a GALFAN bath in the laboratory

The solubility of Ce and La in a GALFAN bath was examined. Figure 3 shows the test procedure. Figure 4 shows the concentration of Ce and La at 10 cm below the GALFAN bath surface. When a GALFAN bath is stirred sufficiently, the concentration of Ce and La is homogeneous. However, under a static condition, at the same point, the concentration of Ce and La decreases, and 2 hours later, the concentration value seems to reach its solubility. Figure 5 shows the concentration of Ce and La at 10 cm below the GALFAN bath surface at 3 hours later at various temperatures. From Figure 5, the solubility of Ce and La might be 0.005 wt% and 0.003 wt% at 450 °C. Consequently, excess mischmetal seems to sink and accumulate at the bottom of the crucible.

5. Analysis of a GALFAN bottom dross

A compound in a GALFAN bottom dross was analyzed as follows:

The microarea quantitative analysis of the cross-section sample was carried out by the standardless ZAF correction method using the Kevex delta-V, after counting the X-ray spectrum

by use of the Field Emission-Scanning Electron Microscopy / Energy Dispersive X-ray Spectrometry (FE-SEM/EDS, Hitachi model S-4100), which was operated at an acceleration voltage of 15 KV.

Photo.4 shows the SEM image of a GALFAN bottom dross. A number of the compounds exist in the GALFAN bottom dross. The diameter of the compounds is about 150 μ m. The compounds are composed of 3.1at%Ce, 3.3at%La and 0.4at%Nd (6.1wt%Ce, 6.5wt%La and 0.8wt%Nd) involved in Zn. If this phase is an intermetallic compound, it nearly corresponds to Zn₁₃Ln (Ln stands for mischmetals) in Zn-mischmetals phase diagram (Figure 6). However, Zn-mischmetals intermetallic compounds evidently still have not been proved, for example, the JCPDS does not correspond to the phase diagrams exactly. Therefore, considering quantitative error, this phase might be Zn₂Ln or Zn₁₁Ln.

Moreover, though a X-ray diffraction analysis was carried out, the phase couldn't be identified exactly.

6. Mechanism of the granular-shaped dross defect formation and Discussion

As mentioned above, regarding a granular-shaped dross defect, the following is demonstrated:

- (1) A granular-shaped dross defect on a galvanizied steel has nuclei composed of Zn, Ce and La.
- (2) Ce and La are involved in a GALFAN bath. The solubility of Ce and La is respectively 0.005wt% and 0.003wt%. The excess Ce and La exist as an Zn-Ce and Zn-La (Zn-mischmetal) intermetallic compounds. Therefore, most of Ce and La in a GALFAN bath sink and accumulate at the bottom in the main pot. An intermetallic compound in a GALFAN bottom dross is composed of 3.1 at%Ce, 3.3at%La and 0.4at%Nd (6.1wt%Ce, 6.5wt% La and 0.8wt%Nd) involved in Zn. In exchanging the GALFAN bath into a regular galvanizing bath, some mischmetal dross remains in the main pot. Ce and La in a regular galvanizing bath rise gradually.
- (3) The intermetallic compound size is $\sim 50 \,\mu$ m in a GALFAN production bath, $\sim 200 \,\mu$ m in a GALFAN bottom dross and $\sim 200 \,\mu$ m in a regular galvanizing bath.

Thus, the mechanism of the granular-shaped dross defect is deduced as follows:

- (a) Excess mischmetal exists as an Zn-mischmetal compound and accumulates as bottom dross in a GALFAN bath (Figure 7A, 7B).
- (b) In exchanging the GALFAN bath into a regular galvanizing bath, since some GALFAN bottom dross solidifies, GALFAN bottom dross cannot be removed completely (Figure 7C).
- (c) The mischmetal dross residue which remains in the main pot gradually rises in the regular galvanizing bath (Figure 7D).
- (d) The floating Zn-mischmetal intermetallic compound in the regular galvanizing bath attaches to the steel strip and becomes a granular-shaped dross defect.

The density of the Zn-mischmetal intermetallic compound might be $6.9 \sim 7.1 \text{ g/cm}^3$ because the compound sink in a GALFAN bath(6.9 g/cm^3) and float in a regular galvanizing bath (7.1 g/cm³).

Regarding the reason GALFAN doesn't have granular-shaped dross defect, two reasons are possible. One is that a Zn-mischmetal intermetallic compound in the GALFAN bath is smaller ($\sim 50 \,\mu$ m) than that of a regular galvanizing bath ($\sim 200 \,\mu$ m). The other is that the intermetallic compound is more easily wiped off the steel strip in a GALFAN bath since the viscosity of a GALFAN bath is smaller than that of a regular galvanizing bath.

7. Preventive methods against granular-shaped dross defects

Basically, a granular-shaped dross defect is caused by an excess mischmetal addition into a GALFAN bath. Therefore, the decrease of the mischmetal addition appears to be most effective. Mischmetal prevents bare spots on GALFAN steel sheets. However, effective mischmetal seems to be up to the solubility in the GALFAN bath. Sumitomo decreased amount of mischmetal from 0.1wt% to 0.05 wt% at first. The GALFAN bottom dross decreased and the GALFAN steel sheets still had good surface appearances. In addition to the decrease of mischmetal, Sumitomo removed GALFAN bottom dross in the main pot as much as possible and scraped dross off with a stabilizing and a correcting roll. As a result, the granular-shaped dross defect on regular galvanized steel sheets has almost been eliminated.

Since the solubility of mischmetal in a GALFAN bath at 450 °C is about 0.01 wt%, Sumitomo will decrease mischmetal furthermore paying attention to bare spots on GALFAN steel sheets.

8. Conclusion

Sumitomo has experienced granular-shaped dross defects on regular galvanized steel sheets at Wakayama No.2 galvanizing line. The granular-shaped dross defect has nuclei composed of Zn, Ce, La. Excess mischmetal exists as Zn-mischmetal intermetallic compound, and forms bottom dross in a GALFAN bath. The bottom dross residue becomes top dross in the regular galvanizing bath and causes surface defects.

The residual mischmetal dross problem has almost been solved by decreasing mischmetal in a GALFAN bath, removal of GALFAN bottom dross and scraping with a stabilizing and a correcting roll. Sumitomo will decrease mischmetal furthermore paying attention to bare spots on GALFAN steel sheets.


PECMUE Application of the second sec second sec



Photo.2 A cross a film SEM rick grighted a granular waget in as 1 to the analysis of a granular WAV available.





Table 1 Mischmetal components.

				(wt%)
Ce	La	Nd	Pr	S m and others
50	30	15	4	1

Sampling procedure

(wt%)

(P: Pump

GALFAN			Galvaniz	red	
ST	ART	→	END	START →	•
No. 1	No. 2	No. 3	No. 4	No. 5	

Table 2 Concentrations of Ce and La in the main pot.

Bath exchange

No.	Bath	Condition	Tor)	1m be	elow	Bott	on
			Ce	La	Ce	La	Ce	La
$\overline{1}$	GALFAN	static	0.003	0.002	0.004	0.002	-	-
2	GALFAN	line speed 36m/min	0.008	0.003	0.009	0.004		
3	GALFAN	line speed100m/min	0.037	0.014	0.041	0.015	-	-
4	GALFAN	bottom dross	-	-	-		2.902	1.086
5	Galvanized	line speed100m/min	0.028	0.013	<u>]0.018</u>	0.008	-	



Figure 2 The concentration decrease rate of Ce and La in the top dross and the top of the regular galvanizing bath.







Figure 3 Experimental procedure in the laboratory.



Figure 4 Concentrations of Ce and La in the GALFAN bath at 460℃.



Figure 5 The solubility of Ce and La in the GALFAN bath (3 hours later).



Photo. 4 A cross section SEM micrograph of a GALFAN bottom dross.



Figure 6 La-Zn binary phase diagram.



Figure 7 The distribution of Zn-mischmetal intermetallic compound in the main pot.

XIII-10

<u>DuBois:</u>	Have you ever checked your new alloy to see if you already have drosses in the ingot?
<u>Ueda:</u>	Yes. We have found intermetallic compounds consisting of Zn-Al and mm in particles up to 10 μ m. We then find Zn-mm intermetallic compounds in the bottom dross.
<u>DuBois:</u>	Why do you have such a high concentration of mm? You said you use 0.1%. That is very high.
<u>Ueda:</u>	What do you use?
<u>DuBois:</u>	We use very low. We started with 200 ppm and found it was too high, over solubility.

XIII-12

.

Report From Bath Management Task Force

Presentation by M. DuBois, Task Force Chairman

Presented at the

17th Galfan® Licensee Meeting

October 1992

Tokyo, Japan

COCKERILL

BRANCHE PHENIX

DIRECTION TECHNIQUE

AMELIORATIONS PHYSIQUES ET METALLURGIQUES

MDU/sra/894

MANAGEMENT = Define actual position Make correction in order to keep the set point

POT ANALYSIS

> SAMPLE OF LIQUID METAL : Homogeneity of composition -> (Where How

> > Segregation during solidification -> (Method Procedure

> > > Problem with drosses trapped

ANALYTICAL METHOD :

CASTING :

Accuracy and reliability -> { Method Procedure

EVOLUTION OF COMPOSITION

<u>OBJECTIVE</u>: A] <u>CONSUMPTION OF AI, La, Ce</u> by drosses sheet pumping procedure

- * DROSS : Type (top, bottom) Homogeneity of composition Level of Al, La, Ce, Fe
- * SHEET : Reliability of Al content (pickling problem)
- * PUMPING : Loose of La and Ce

- -> Check
- -> Analyse
- -> Procedure
- -> Confirmation Explanation

EVOLUTION OF COMPOSITION

OBJECTIVE : B] LOADING OF AI, La, Ce : EFFICIENCY OF INGOTS

- AI: Level of ingot composition Reliability of AI content in ingot AI efficiency (if 15 %, 5 %) How to enrich the bath
- -> best level

La] : Level of ingot composition -> special alloy Ce] How to reenrich the bath

General : weight of ingot -> objective 1 T

WORKING METHOD

PRINCIPLE : Working groups Exchange of results Free of additionnal cost

CONDITIONS FOR PARTICIPATION :	active producers
	(> 5000 T sheet/Y)

- . active alloy supplier
- **MEETINGS**: When: . 2 */Y (1 is annual Gf meeting)
 - Where: . by 1 producer, different each time, 3 zones
 - Cost: . free except travel
 - Content : . echange of practical results . define the job and objectives of each member for the next 6 months
 - Assistance : . 2 poeple max.

OBJECTIVES :	Define : .	analysis procedure for bath dross and coating (for Al eff, La, Ce, Fe)
		ingots to load
		La, Ce, Al reenrichment.
<u>WORK</u> : .	Everybody is working	ng
	GF producers :	. follow campaigns
		. prepare and make samples
	Alloy suppliers :	. analysis
		. evaluation of method reliability
	La, Ce, suppliers	: . assistance for analysis of La, Ce
•	Duration: 2 to 3 y	ears minimum.

QUESTIONS AND ITEMS TO THINK ABOUT

* ZINC POT MANAGEMENT

- La and Ce may be lost during pumping : well known ?
- Fe increases during compaign, to level equal to Gi : how much ?
- . Fe and La in the pot seem to be in relation : confirmation ?
- . Drosses : composition and amounts ?
- . Al to load seems to be higher than Al in pot : Al balance ?
- . Define effective Al
- . Sampling and analysing method : ICP Titration ...
- . Analyse of coating Pickling method
- . Type of ingot for pot enrichment Jumbo Composition
- Bath segregation

PITTSBURG 91

ABSTRACT

Laboratory testing and field start-up experience have confirmed again that steel which is clean enough to galvanize regularly is not necessarily clean enough for Galfan. Inadequate cleaning continues to be the most often encountered cause of coating defects. This report will discuss the ways in which cleaning can be improved for Galfan galvanizing including formulation of the cleaner, high current density, scrubbing and ultrasonic methods.

INTRODUCTION

To achieve good wetting and necessary adhesion for Galfan coating, the steel surface must be clean and free from oxides. Reduction of oxide film and burning off (at least partially) soil is usually provided by heating the steel strip, tubing, wire or part in reducing atmosphere. Industry has ample experience in running lines with such technological scheme. But attempts to use conventional flux for this purpose failed, black spots (bad wetting) were observed. The solution to this situation was found by using thin layer of electro-deposited zinc with or without conventional flux. But this electroplating technique, known as Electroflux, demands much greater surface cleanliness.

This report analyzes cleaning, pickling, and electrofluxing procedures for steel surface prior to Galfan coating.

reducing atmosphere, burns off some amount of soil from the surface and demands for cleanliness are relatively low and corresponds to 1-3 μ g/cm² (microgram). Before electroplating amount of soil should not exceed 0.2-0.6 μ g/cm², otherwise adhesion will be poor and some areas might not be covered with electrolytic zinc, which results in black spots during Galfan coating.

Cleaning procedure (choice of cleaner and its concentration, solution temperature, method of cleaning) depends on steel surface dirtiness. Usually amount of soil varies over wide range—from 10 to 100 μ g/cm² and even more. Soil contains mineral and/or vegetable oil, animal fat, graphite, minor particles of iron, sometimes bearing grease.

It is unrealistic to look for a miracle cleaner formulation which removes any amount of soil from the steel surface in no time and without additional efforts; miracle is impossible.

The heavier the soil, the more concentrated the cleaner solution, higher temperature and more time are required to remove it. Mechanical action like agitation, sprays, scrubbing, and ultrasonic all shorten the cleaning time; especially effective is electrocleaning.

To outline the general idea about possibilities of different cleaning procedures, let us analyze Table One.

Cleaning Time	Up To 10	20-30	50-100		
1-2 min.	Soak	Soak with agitation	Soak with agitation or sprays		
3-5 sec.	Scrubbing by brushes or high pressure sprays	Electrocleaning	Electrocleaning with scrubbing		
1-2 sec.	Electrocleaning	Electrocleaning with scrubbing	Precleaning, Electrocleaning with scrubbing		
0.3-0.6 sec.	HCD* Electrocleaning	HCD electrocleaning Plus scrubbing	Precleaning HCD electrocleaning with scrubbing.		

*HCD - High Current Density

If several minutes may be spent on cleaning procedure, then the heaviest soil could be removed only by soak with agitation. But when time is counted by seconds, more forceful cleaning methods must be used, including mechanical action, electrocleaning and even two stage cleaning. It should be understood that this data is approximate and depends on steel surface anamnesis, oil used, amount of graphite and iron particles, etc.

For cleaning procedures powder or liquid high alkaline cleaners are used. Liquid form makes cleaner handling much easier, especially for automatic replenishing of cleaning solution by its conductivity. Specific gravity of average liquid cleaner is 1.4-1.5, alkalinity - 40% (calculated as sodium hydroxide). By customer request the cleaner can be formulated with very low freezing point - down to minus 20°C, which makes it possible to ship it and keep outdoors in winter time. As builders, which promote cleaning ability

adhesion problems may arise. This is true only it inadequate picking procedure is used.

Concentration of cleaner depends on surface dirtiness and cleaning procedure and varies from 3 to 6%, which corresponds to 1.2-2.4% alkalinity of working solution. For high current density electrocleaning, where high solution conductivity is a must, concentration may be even 8%. The same concentration of cleaner is used for soak cleaning.

Working solution is usually heated up to $80-95^{\circ}$ C. Current density for conventional electrocleaning is 2.5-10A/dm², for high current density cleaning, 50-100 A/dm². To obtain clean surface from 12-30 Coulomb/dm² should pass (1 Coulomb = 1 amp X 1 sec.), depending on initial surface contamination.

Comparative cleaning performance of silicate-free cleaner depending on its concentration for different cleaning modes is shown on Fig. 1.

As cleaning proceeds working solution accumulates soil. When oil amount reaches 1-2%, redeposition of soil on clean steel surface may occur and then tank should be dumped. Usually it takes 2-3 months running on 3 shift base. Our investigation showed possibility to increase cleaning tank life using microfiltration (pore size - $0.2 \mu m$). All suspended solids and 30% of oil can be removed, but filtration does not make the solution life indefinite.

Electrolytic cleaning process for steel strip, tubing, or wire are mostly bipolar. The steel strip is sandwiched between even pairs of grids, made of stainless steel, with polarity changing from one pair to the next. Typical cleaning tanks have 2-8 pairs of grids with cleaning time 0.3-3 sec (lower figure refers to HCD cleaning). Power supply should have voltage 20-30V and amperage depending on simultaneously cleaned surface (from 400 to 24,000A).

and provides required cleanliness of the surface. Our experience with 6-12 mm tubing coils proves that.

Careful removal of cleaning solution by air knife or squeezing rolls is very essential. Intensive rinsing is required after cleaning.

Black spots in the Galfan coating are symptoms of dirty surface. Bad cleaning also contributes greatly to the Galfan coating roughness.

Pickling and Rinsing

Pickling must remove the oxide film from steel surface before electroplating. Usually 10-20% solution of hydrochloric acid is used at ambient temperature. It is necessary to underline, that pickling solution does not remove residual soil from the surface in the case of bad cleaning. For this purpose, special surfactant package should be added (there are so called acid cleaners). But at certain level of solution contamination by oil its redeposition on steel will take place. So cleaning procedure should be adequate and no oil should be transferred into the pickling solution.

If oxide film on steel is thick (it happens often in wire manufacturing), or silicated cleaner was used, then conventional pickling during short period of time (0.5-3 sec) is not enough and electropickling is recommended. Hydrochloric acid solution may be used at current density 10-100 A/dm². There are indications that sodium chloride solution at pH6 can be used as well for pickling. In this case continuous filtration for iron hydroxide removal should be maintained. Solution may be used indefinitely with sodium chloride replenishing to compensate drag-out.

Good rinsing after pickling is important but not critical, because plating tank pH has tendency to raise and must be lowered periodically.

Zinc Electroplating (Fluxing)

As it was mentioned above, zinc electroplating (fluxing) helps to eliminate bad wetting of steel by Galfan alloy, that is, avoid black spots.

Properly cleaned and pickled steel surface should be protected by thin zinc layer prior to be immersed in molten alloy. Thickness of zinc coating has to be $0.4-0.5\mu m$, though there are some indications that even $0.2-0.3\mu m$ for tubing provide no black spots.

It is known that zinc chloride electrolyte has low covering ability, that is, during electrodeposition zinc does not form a continuous film over steel surface, but tends to grow as separate crystals (dendrite). This zinc electrodeposit would not fulfill its destination—to protect steel surface from oxidation and create metallic bonds with alloy.

So special organic additives are put into electrolyte, so called grain refiners. Being adsorbed more readily on zinc crystals than on the iron atoms organic molecules increase over-potential of $Zn^{2+} + 2e \rightarrow Zn^{\circ}$ reaction and tend to create continuous nonporous zinc layer. But this adsorption has physical character and at temperature over 50°C desorption takes place. This is the limit of temperature for electrolyte running, because over 50°C organic additives become inefficient and zinc again crystallizes as porous layer. There is a lot of organic additives which create strong bonds with zinc (chemical adsorption) and do not desorb at high temperature, but they create porous electrodeposition [2] and do not help in Galfan coating.

efficiency (less than 96%), higher causes zinc hydroxide precipitation and creates surface roughness. Plating is done at high current density - 50-100A/dm² and to avoid burn spots, electrolyte should be agitated. This is achieved by strip (tubing, wire) movement through plating tank with high speed (1-3 m/sec) and by pumping electrolyte in the strip-electrode gap, which usually does not exceed 50-75 mm.

Pure zinc bars or granules in titanium mesh basket are used as anodes. Anodic efficiency of zinc plating is more than 100% due to chemical dissolution of metallic zinc in electrolyte. But zinc chloride balance in tank is maintained rather accurately because of electrolyte drag-out with strip or wire. Other components of electrolyte, and mainly grain refiners should be added continuously on Amp.-hrs basis preferably automatically by bath-minder. Solution pH increases very slowly and may be corrected once a shift (Fig. 2).

There is tendency to use insoluble (graphite) anodes for zinc electroplating. We have experience with some plants and many say it is rather inconvenient. Though zinc in solution (to replenish consumed zinc by electrodeposition) is cheaper, than as metallic bars, electrochemical process becomes very unstable. Oxygen and chlorine emanate at the anode and pH drops very quickly (Fig. 2). Continuous addition of ammonium hydroxide by pH-minder (regulator) is needed to keep pH at proper level. But quality of zinc coating is good enough to provide high wetting by Galfan alloy.

It is highly desirable to filtrate electrolyte to avoid surface roughness. This electrolyte may be run practically indefinitely.

After electroplating solution should be removed from the strip by squeezing rolls or air knife.

damage sometimes conventional flux may be additionally applied. This procedure is practiced at Martins Ferry, Wheeling Pittsburgh plant for 48" strip before dipping into Galfan alloy.

Conclusions

1. Careful cleaning of steel surface has critical importance to get good adhesion, smoothness of Galfan coat and avoid black spot (bad wetting).

2. Electropickling of cleaned steel surface is preferable.

3. Thin electrocoated zinc layer provides good adhesion and wetting ability of steel surface by Galfan alloy.

References

1. Michael R. Morin, 16th Galfan Licensee meeting, October 4, 1991, Pittsburgh, PA, USA.

2. Yum Gerenrot, L.P. Kovalchuk, L.Z. Goldin, <u>Journal of Applied Chemistry of the</u> USSR, No. 2, pp. 347-350 (1977).





Performance of Various Methods with Phosphated Cleaner

Leroy:	Does the efficiency of the electro cleaning system depend on whether the steel substrate is cathodic or anodic?
Gerenot:	Usually, pairs of electrodes are used with the polarity alternating so the steel substrate alternately is cathodic then anodic. This is the system we use most. If, however, you want to use one rectifier for both cleaning and pickling, then it would probably be better to make it cathodic because twice the gas.
Leroy:	I suppose in the first case, you must switch polarity from time to time.
Gerenrot:	Yes. We do that to clean the electrodes.
Leroy:	What we observe is that the final pollution of the strip depends on the anode-cathode sequence.
Gerenrot:	No, it does not make any difference. In typical electroplating practice, it is usual to make the last electrode anodic so that a thin oxide film is removed during pickling but in our case, we use more pairs of electrodes so that there is no significant difference.
Leroy:	How often do you change the polarity of the electrodes?
Gerenrot:	Every three to four hours.
Leroy:	Did you consider carbonization in the cleaning section?
Gerenrot:	What do you mean by carbonization?
Leroy:	The CO_2 trapped in the air in the cleaner which changes the pH and activity of the cleaner.
Gerenrot:	I have not seen the problem. We recommend monitoring the electrical conductivity of the cleaning solution and making corrective changes manually or automatically.
Leroy:	Okay. Then you compensate by adding cleaner to maintain the conductivity. Now, another point. What is the influence of the silicate?
Gerenrot:	I will not go into the mechanism but I will explain what it does. Silicon is a very good builder. It makes the cleaner very effective to remove non-organic soils such as particles of carbon, iron, etc. I think silicated cleaners have a good future because they are environmentally friendly.
Leroy:	I agree but the drawback is that they leave a silicate film on the surface.
Gerenrot:	Yes. I stressed that if silicate cleaners are used, you must also use vigorous electro pickling.
Leroy:	Do I understand you have some nickel in the electroflux solution?

	of ons and non.
Gerenrot:	We have not had a problem with iron affecting the efficiency of the cleaner. Typical Fe contents would be, let's say, 50ppm to 100ppm.
Dubois:	You are talking about the dissolved iron but what about the iron in suspension?
Gerenrot:	You must filter it out.
Dubois:	The iron fines are so small, 2 to five microns, it is not easy to filter them out of the solution. What do you recommend?
Gerenrot:	We use a scheme called <i>cross-section filtration</i> which uses a membrane-type media in a side-stream unit and is capable of removing the iron fines. It cannot, however, remove imulsified oils.
Dubois:	What do you do then to remove the oil? We have had bad cleaning problems when the oil content gets to 2-4 g/l.
Gerenrot:	One way is to damp the tank but this practice is not popular so the other way is to use a pre-cleaner which will remove the oil, then to let it float to the top where it can be skimmed or separated into another tank.
Leroy:	Did you consider the problem of hydrogen gas entrapment in all these electrolytic processes?
Gerenrot:	This is a good question. It is a problem. There is much literature on this subject. The GALFAN lines we have experience on do not have long exposures, maybe one second or so and we have not seen signs of hydrogen entrapment.
Leroy:	Maybe in your preheat before dipping it is released.

Presented by John M. Rendos, Superintendent-Technology

Wheeling-Pittsburgh Steel Corporation

Martins Ferry Plant

Martins Ferry, OH USA

17th Galfan Licensee Meeting

Keidanren-Kaikan International Conference Hall Tokyo, Japan

October 12 - 14, 1992

widths from 27.125" (689 mm) to 48.000" (1219 mm) were coated. A second trial production run commenced on May 8, 1992 entailing some 300 tons (272 metric tons) of substrate to be coated. Here eight (8) different gauges from .0153" (.39 mm) to .057" (1.45 mm) across four (4) different widths from 27.250" (689 mm) to 48.000" (1219 mm) were coated. A third trial production run commenced on August 21, 1992 entailing some 300 tons (272 metric tons) of substrate to be coated. A third trial production run commenced on August 21, 1992 entailing some 300 tons (272 metric tons) of substrate to be coated. Here eight (8) different gauges from .0143 (.36 mm) to .057" (1.45 mm) across seven (7) different widths from 27.250" (689 mm) to 48.000" (1219 mm) were coated. Coating weights ranged from GF20 (61 gm/m²) to GF210 (640 gm/m²). Commercial production is scheduled to commence late fourth quarter 1992.

II. LINE CONFIGURATION

The Martins Ferry Plant operates three (3) Cook-Norteman (flux) galvanizing lines and utilizes a hot rolled, full hard, or pre-annealed product for galvanizing.

Our 48" (1219 mm) line contains an entry section for joining coils, including two (2) expanding entry mandrels, Taylor-Winfield welder and side trimmers. This is followed by a vertical accumulator, a cleaning section with alkali and hydrochloric acid cleaning, a vertical plating cell, and a flux tank for preparing the strip for entry into drying and preheat ovens. The balance of the line is similar to all galvanize lines, containing a refractory lined electric inductor heated zinc pot and associated coating equipment, a cooling tower, tension leveler, chromating treatment unit, vertical accumulator and a delivery section for recoiling. The typical line data is shown in Table I.

III. INITIAL LINE MODIFICATIONS

- Removal and renovation of the rinse and flux tank area, including the addition of a new cascade rinse system.
- Manufacture of soluble zinc anodes.
- Manufacture of a stainless steel sink rig.
- Addition of a plating cell, rectifiers, storage tanks, electrics and associated equipment.

XVI-2

- Two (2) 26,000 amperes, 20-volt plating rectifiers (top and bottom).
- Four (4) anode bridges, two (2) bridges for top anodes and two (2) for bottom anodes.
- Thirteen (13) anodes 4 inches (102 mm) wide by 3 inches (76 mm) deep with approximately 5 feet (1.5 m) active faces under the plating solution level are used at each bridge. Total width coverage is 52 inches (1321 mm).
- Initial plating cell electrolyte make-up consisted of Zinc Chloride Potassium Chloride solution.
- On August 6, 1992, the plating cell electrolyte make-up was changed to a Zinc Ammonium Chloride solution.
- Plating cell and holding tank capacity is 5,000 gallons (18,925 liters) with capability to heat or cool solution to maintain electrolyte temperature.
- Plating cell solution is constantly filtered and recirculated at a rate of 500 gallons per minute (31.5 liters per second).

IV. PROBLEMS ENCOUNTERED DURING GALFAN PRODUCTION

The Martins Ferry Plant had encountered the following problems during Galfan production:

- A. Extended time required to switch over from normal hot dip zinc coating to Galfan and vice versa.
- B. Bath chemistry variation and deterioration.
- C. Generation of uncoated and black spots.

- High grade zinc is charged through the premelt some 12 to 15 turns prior to the Galfan run. Purpose is to drive lead concentration of the normal zinc bath as low as possible so that in building the Galfan bath, lead concentration will be 100 ppm or less. Die cast (10% Al) is also charged to maintain pot Al. Product mix is important here due to the loss of spangle.
- One week before a Galfan run, one acid tank is dumped, cleaned and recharged.
- Three turns before a Galfan run, the following steps are taken:
 - A. The remaining acid tank and the alkali tank is drawn, cleaned and recharged. Scrubber brushes and squeegee rolls are changed.
 - B. Flux tank is pumped out into totes, cleaned and recharged with Zaclon ZR flux. New flux brushes are installed.
 - C. The 180-ton (163 metric ton) HDG pot is drossed.
 - D. Pumpover 120 tons (109 metric tons) of HDG (low Pb) metal into holding pot. At that time, remaining metal will be down to the throats of the inductors.
 - E. At the end of the pumpover, the main pot is charged with 1,250-pound (17.6 kg) sows of Galfan metal and four (4) lifts of Galfan metal through the premelt.
 - F. During this time, inductor heating action and routine preventive maintenance procedure of blowing inductors with N_2 lances are utilized to maintain agitation.
 - G. Cleaning section concentrations and temperatures are brought up to operating levels.
 - H. All maintenance welds including threading of the plating cell are performed.
 - 1. One hour before startup the stainless steel rig is set, including the stabilizer roll.

 At the end of the Galian campaign, approximately one turn is needed to pump out Galfan metal into chills, set rig, adjust flux, remove strip from plating cell, and recharge main pot with metal previously pumped to the holding pot.

VI. PRODUCT TESTING RESULTS

A. <u>Pot Chemistry</u>

- The pot chemistry of the September, 1991 Galfan campaign was erratic and showed deterioration of Al, Ce and La. Probable cause was large amount of bottom dross present during the first campaign. Since that campaign, no bottom dross has been visible and that portion of the problem has been eliminated.
- The addition of N₂ lances into the bath for constant agitation has also been a benefit.
- The effects of the flux and subsequent generation of top dross and skimmings are currently being evaluated.
- Wheeling-Pittsburgh Steel will be an active participant in the North American Bath Management Task Force set up by ILZRO.

B. Black/Uncoated Spots

- Metallographic and SEM analyses have led to the elimination of the Potassium Chloride electrolyte and the usage of Zinc Ammonium Chloride as the electrolyte.
- Benefits included the elimination of Potassium Chloride crystal precipitation out onto the strip during plating which generated uncoated spots. Temperature control, although still critical, is much more readily attainable; 130°F (54°C) max. versus 140°F (60°C) to 150°F (65.5°C).
- Electrolytic deposition of zinc although the same (.4 µm/ft.² per side) for both the Potassium Chloride and the Zinc Ammonium Chloride, SEM zinc dot map analysis has shown the latter to be a much more consistent and even coating.

- I emperature, Baume and consistency of application is also pivotal.
- Some preliminary work is being done in oven heating practices and controls as a possible source of uncoated spots.
- Black spots due to the formation of Aluminum Chloride compounds on the surface of the Galfan coating have been minimal.
- Cleaning of the strip has been found to be crucial and can be a primary contributor to uncoated spots. Electrolytic deposition of zinc in the plating cell will be adversely affected instantly. Much work to be done in this area.
- The addition of a hold down roll on the south conductor roll of the plating cell and spray headers on the conductor rolls to keep them wet has eliminated arcing and the resultant uncoated spots.

C. <u>Surface Appearance</u>

- Coating weights of GF60 (183 gm/m²) and lighter have good smooth surface appearance.
- Coating weights of GF90 (274 gm/m²) and heavier have sag lines and, although greatly diminished during the May and August 1992 campaigns, would not have a suitable appearance for painting.

D. <u>Microstructure</u>

- A mixed eutectic microstructure with a greater percentage of the Zn-Al eutectic than the pure zinc.
- The May, 1992 and August, 1992 runs revealed the pure zinc spheroids to be predominantly at the Galfan-substrate interface with the Zn-Al eutectic at the surface of the Galfan coating.

HDG steel. These same results were also achieved on full hard material.

- The brittle alloy layer is minimal. Iron in coating values typically are in the 30 to 50 mg Fe/ft.² range even on full hard products.
- In the 180° zero-T bend test, no cracking occurred.
- Similar good conditions were obtained from Lockformer tests.
- Paint trials on full hard .0153 inches x 41.250 inches (.39 mm x 1048 mm) agricultural roofing and siding material have gone very well.
- During the paint trials, typical paint evaluation tests performed exceeded expected performance and were superior to normal galvanized sheet processed at the same time.
- The lack of cracking or crazing of the paint film during deformation as evaluated by 80 inch-pound impact tests, bend tests, and actual roll forming was outstanding.

VII. <u>CONCLUSION</u>

After our initial Galfan campaign of September, 1991 and the two subsequent trial campaigns of May, 1992 and August, 1992, and after incorporating changes in practices and modifications to equipment, Wheeling-Pittsburgh Steel Martins Ferry Plant has been successful in coating Galfan on a Cook-Norteman (flux) hot dipped galvanizing line. Obviously, many refinements of the initial production line and technology have taken place in the short eleven month time span encompassing the three trial production runs totalling some 1,800 tons (1,633 metric tons).

We at Wheeling-Pittsburgh Steel have acquired a great deal of technical information on the production of Galfan through presentations and discussions with various Galfan licensees and suppliers which has been essential to our success. However, much is left to be learned and accomplished in the area of technical improvements. We would like to thank all members of the meeting. improvolution

Capacity	226,800 tons/year	205,700 metric tons/year	
Line Speed	370 feet/minute	114 meters per minute	
Strip Dimensions	.014"079" thickness 22" - 48" width	.36 - 2.00 mm thickness 559 - 1219 mm width	
Coil Weight	40,000 lbs. max. 72" maximum O.D.	18,150 kg max. 1829 mm maximum O.D.	
Coatings	Zn (regular spangle) and Galfan		
Surface Treatment	Chromated, oiled, chromated and oiled		

•


SEM zinc dot map of an as-plated coupon utilizing the Potassium Chloride - Zinc Chloride electrolyte. The dark areas indicate an absense of zinc deposition ar at best minimal zinc deposition.



SEM zinc dot map of an as-plated coupon utilizing the Zinc Ammonium Chloride electrolyte. Notice the evenness of the zinc deposition.



Electron photomicrograph at 200x showing a defect (cross section) which is seen to include an uncoated area. Note the thin white line of Potassium crystals near the base of the defect area.



Electron photomicrograph at 1500x showing the Potassium crystal layer seen in the previous electron photomicrograph



Electron photomicrograph showing a defect which initially appeared to be an uncoated spot. SEM analysis confirmed high concentrations of AL and CL in the black spot.



Macrophotograph of what we termed a "bullseye" defect which we believe was due to arcing from the plating cell. Center area is an oxide layer. Note the expanded circular area around the uncoated spot.



Photomicrograph (cross section) at 100x through possible arcing burn. Notice the absense of GALFAN on the bottom. Also notice to the left the dark oxide layer which has formed and actually projects beneath the GALFAN layer. Some changes in microstructure top and bottom can also be seen.



Microstructure at 100x of the first GALFAN campaign on September 26, 1991



Microstructure at 1000x of the first GALFAN campaign on September 26, 1991



Microstructure at 100x of the second GALFAN campaign on May 8, 1992.



Microstructure at 1000x of the second GALFAN campaign on May 8, 1992.

	1
•	
	2
	1
	1
	J

Microstructure at 500x of the third GALFAN campaign on August 21, 1992

.

XVI-14

Capul:	What is the normal lead level in your galvanizing bath?		
Rendos:	Our normal Pb level for galvanizing is about 900 ppm.		
<u>Chairman:</u>	Do you know what the GALFAN's Pb level was in your GALFAN campaigns?		
<u>Rendos:</u>	We were able to reduce them to 100ppm and we think we can reduce that even more. By running 12-15 turns of SHG zinc for galvanizing just before converting the line to GALFAN, the final galvanizing bath is about 350 ppm which produces a minimized spangle which may be objectionable to a customer who wants unpainted but which can be used nicely for our pre-paint orders. We also found a tendency for the galvanizing coatings to have a rough, sandy appearance during the low Pb production but corrected the problem by raising the bath temperature to $860^{\circ}F$ (460°C).		
<u>Dubois:</u>	Do I understand that you start the GALFAN campaign with a lot of galvanizing dross?		
Rendos:	Only the first campaign. First, a cook-Norteman flux line does not generate much bottom dross, so that what dross was there for the first campaign was more than a year's accumulation since. If we run GALFAN on a quarterly basis, we think galvanizing dross will not be a problem anymore.		
Dubois:	Why are the campaigns so small?		
<u>Rendos:</u>	We did not expect the first campaigns to be without problems so we ran only enough to identify the problems. The next campaign (January, 1993) is scheduled for 12 turns and we think we have identified all of the problems and made short-term corrections to allow us to expect all of the product will be prime.		
Dewitte:	What is the flux you use?		

	means defective adhesion.	
Dewitte:	Are you not using the flux described in the previous paper by J.D. Hostetler?	
<u>Rendos:</u>	Yes. We are using that same flux (FGF-95W) he describes in the electroflux cell and will probably use it in the dunk flux tank in the future. (Wheeling-Pittsburgh's arrangement includes two flux applications; an electroflux followed by an additional dunk/spray flux).	
Wiliams:	You mentioned the use of your mini-spangle rig (using air only). What sort of cooling rate does it provide?	
Rendos:	We have no way of measuring so we really don't know.	
<u>Williams:</u>	When you change back to regular galvanizing, how do you adjust the Al in the bath?	
Rendos:	We pump nearly all of the GALFAN out. Some small amount freezes on the sides of the pot and a small heel is left on the floor so that the Al content of the new galvanizing bath is about 0.2% which is higher than our normal 0.12%. We then schedule full hard product which uses up Al faster and in 3-4 turns we return to normal levels.	
	We share the concerns for better cleaning. Our line was built in 1955 and the cleaning section has not been significantly improved. It does a very acceptable job for regular galvanizing but as already stated in other reports, the degree of cleanliness is more demanding for electroflux so we are considering conversion to electrolytic cleaning.	

An accurate analysis of GALFAN-coatings show, that the amount of the elements Ce and La within the coating are very small in comparison to the bloc contents and to the content of the bath. On the other side we observe that the Al-content is higher in the coating than in the bath. The enrichment of Al at the steel substrate depends on galvanizing parameters so that it is possible that the Al-content in the bath will break down during a Galfan campain (f.ex. little coating weights).

In this context it can be of interest to draw up a mass balance for the different elements Fe, Al, Ce and La. The input of these elements in the bath is very well known (mass and analysis of the GALFAN blocs). The output of these elements is governed by the coating and the formed drosses.

To draw up a mass balance we have to analyse with a high accuracy the samples of the bath, the drosses and the coated strips.

To analyse the samples of the bath and the drosses dont cause any problems They are fully dissolved in diluted HCl and then quantitatively analysed with the ICP-method.

To analyse the coating is more complicated. We have to ensure, that on the one side the whole coating will be dissolved but on the other side that the steel substrate will not be attacked. If we have for instance a coating The principle of our method is very close; only that we need a better accuracy.

The examined surface should be 10 000 mm^2 (5.10 cm; two sides). The sample have to be weighed with an accuracy of 0,01 g and then to be dropped in a beaker containing 40 ml of dilluted HCl (25%) at ambient temperature (22 + 2 °C). More concentrated acid leads to a stronger attack of the steel substrate. The used inhibitor is hexamethylentetramine (C6H12N4) in a concentration of 0,1%.

In our method, the end of the pickling is not determined by the end of the hydrogen formation because at that time some smal black spots (Fe-Al-Zn) remain on the substrate surface which belong to the coating and have also to be dissolved.

The end of the pickling time is to chose identical with the fully disparition of the black spots and is situated a few minutes after the end of the hydrogen formation. Now the sample has to be removed immediatly. We have observed that the used inhibitor is effective, but that he is not able to prevent fully an attack of the substrate (order of magnitude about 1 mg/h at 25% HC1).

Now the sheet-sample has to be rinsed with demineralysed water. A second rinsing with acetone enables a rapid drying. Than the sample is weighed in order to determine the coating weight.

XVII-2

This solution serves for quantitative analysis of the Elements Fe, Al, Ce and La in the ICP spectrometer. The characteristic radiation of the different elements are measured and compared to standarts. An integration of the surface under the obtained peak delivers than quantitatively the amount of the element with an accuracy of 2 - 5 %.

~

W UNION MINIERE

Reference method for analysing GALFAN-coatings

1)	Use a sample with a surface area of 5000 mm²(5*10 cm) and weigh it with an accuracy of 0,01 g.	
2)	Dissolve the coating in 40 ml di luted HCl. 25 % HCl 0,1% Hexamethylentetramine (C6H12N4) 22 °C (+ 2) The end of the pickling corresponds with the fully disparition of black spots on the sheet sample (a few min after the end of H2-formation)	
3)) Remove the sample immediatly and rinse it with demineralysed water. Rinse a second time with acetone to enable a rapid and effective drying.	
4)	Weigh the sample again and determine the coating weight (Weight-loss * 40 = Coating-weight g/m²)	
5)	Add 25 ml H2O2 (30 Vol.) to the pickling solution and bring it to boiling temperature (after 2 - 3 min. eventually formed cements are dissolved).	
6)	Let cool down the solution to ambient temperature; then transfuce into a measuring vessel and fill up to 100 ml (concentration = 10 %).	
7)	Make quantitative analysis of the different elements with the ICP spectrometer	

W UNION MINIERE

The ICP-Method

Princ	<u>iple</u>
The s (Argo the e	olution, which has to be analysed is nebulised in a plasma torch n). Then the intensity of one or more caracteristic spectral lines of lement in consideration is measured.
Used	spectral lines
Fe A1	259.940 nm 396.152
Ce	308.215 413.765 408.671









XVII-8





W UNION MINIERE

Analysis of elements within GALFAN-coating

	Al (%)	Ce (ppm)	La (ppm)
GALFAN-bloc	4,40	100	100
Bath	4,10	95	40
	(4,02-4,26)	(40-180)	(13-80)
Coating	4,17	29	6
	(4,06-4,36)	(13-46)	(1-14)
Drosses	4,47	426	196
	(4,30-4,90)	(230-980)	(120-430)

with a surface area of 5 000 mm², the loss of mass in grams when the coating is dissolved, multiplied by 200, will represent the coating mass in grams per square metre of the product, including both sides.

A.2 Reagent and preparation of the solution

Reagent:

- Hydrochloric acid (HCl ρ_{20} = 1,19 g/cm³)

- Hexamethylenetetramine

Preparation of the solution:

The hydrochloric acid is diluted with deionized or distilled water in the ratio one part pure HCl to one part water (50 \$ dilution). Hexamethylenetetramine is then added, stirring, in the ratio of 3,5 g per litre of dilute hydrochloric acid solution.

This prepared solution permits the execution of numerous successive dissolutions under satisfactory conditions of attack of the coating, both from the point of view of speed and accuracy.

A.3 Apparatus

Balance capable of weighing samples to an accuracy of 0,01 g. For the test, use a take-off device.

A.4 Procedure

The following operations are applied to each sample:

- if necessary, degrease the sample with an organic solvent which will not attack the coating, then dry the sample:
- weigh the sample to an accuracy of 0,01 g;
- place the sample in the hydrochloric acid solution with hexamethylenetetramine inhibitor at ambient temperature (20 - 25 °C). Leave the sample immersed in the solution until the release of hydrogen ceases or only a few bubbles are released;

92/43235 DC XVII-11

Page 20 prEN 10214:1992

- after the attack, the sample is washed and brushed under running water, dried with a cloth and then by heating to around 100 $^\circ\mathrm{C}$ and cooled or dried by blowing with warm air; <u>к</u> н
- weigh the sample again to an accuracy of 0,01 g; ŧ
- determine the difference between the mass of the coated sample and that of the sample without its coating. This difference, calculated in grams, represents the mass m of the coating. ł

demonstrate their benefits for applications in building and appliance industry. In this paper first results on corrosion behaviour will be presented.

Keywords: steel, corrosion, metallic coating, GALVALUME, GALFAN, post-treatment, prepainting, building- and applianceindustry

INTRODUCTION

Since many decades conventional continuous hot-dip galvanizing is being used to provide an effective protective coating for steel sheet. More recently, there have been some efforts to improve the coating's resistance against atmospheric corrosion by adding alloying elements (especially aluminium) to the zinc (1), finally leading to commercial introducing of GALVALUME® (symbol AZ) and GALFAN® (symbol ZA) in 1972 and 1983, respectively. GALVALUME developed by BETHLEHEM Steel Corp., its technology being licensed by BIEC International Inc. is steel sheet protected with a hot-dip aluminium alloy coating with a zinc content of approx. 43.4 %. A small amount of silicon (approx. 1.6 %) is added to the Al-Zn alloy to avoid the formation of brittle intermetallic Fe-Al-Zn-Si layers which may be caused by the reaction of the melt with the steel substrate.

GALFAN developed by CRM (Centre des Recherches Metallurgiques, Liege, Belgium) by order of the ILZRO (International Lead Zinc Research Organisation, USA) is steel sheet protected with a hotdip zinc alloy coating with an aluminium content of approx. 5%. Cerium and lanthanum traces (mischmetall) are added to enhance the wettability of the steel surface.

Production of GALFAN and GALVALUME at HOESCH Stahl AG started in 1984 and 1988, respectively.

There are many applications where the use of GALVALUME and GALFAN can result in a real improvement in performance as compared to conventional hot-dip galvanized steel sheet. This is reflected by the increasing production world wide (2,3). HOESCH Stahl AG produced approx. 84,000 t GALFAN and 31,000 t GALVALUME in 1991 which may be compared with the company's 1991 total output of approx. 750,000 t hot-dip galvanized steel sheet (including GALFAN and GALVALUME). Recent years have seen an increasing proportion of GALFAN going over to coil coating (3). In 1991, 54 % of GALFAN produced by HOESCH Stahl AG was coil coated whereas GALVALUME almost exclusively was delivered in bare condition.

appliance-industry the high reflectivity and thermal stability of GALVALUME should be emphasized thus being suitable for toasters, ovens, heatshields, lighthousings or solar panels. Due to its excellent forming behaviour bare GALFAN is frequently used for parts with exacting formability requirements. Important examples are loudspeaker housings or filter cans, motor and servo brake housings for the automotive industry. Performance of bare GALVALUME and GALFAN often can be improved by a post-treatment. Usually a chromate passivation treatment, or oil if necessary, is applied at the end of the coating line to prevent moisture-induced staining during transport and storage. Only recently, several organic chromate solutions (e.g. Granodine $3960^{\mathbb{R}}$, Brugal GM-4 $^{\mathbb{R}}$) intended for passivating the surface as well as for providing lubricity for dry roll-forming were commercially introduced. Such a sealing also effectively prevents fingerprints and retards formation of black rust during outdoor storage in humid environment which may occur particularly on GALVALUME. Prepainted GALVALUME and GALFAN is used e.g. for roof and wall elements of residential and non-residential buildings, fencing or

elements of residential and non-residential buildings, fencing or rain ware. Moreover, there are numerous applications in the field of the appliance-industry.

The use of prepainted GALFAN is particularly advantageous whenever extremely demanding technical-functional and decorative combined with exacting formability requirements are involved. Examples are shower cabins, indoor-wall and -roof elements. Currently there are even efforts to replace prepainted electrogalvanized steel sheet usually being a preferred base material for these applications.

CORROSION-BEHAVIOUR OF POST-TREATED GALVALUME

During plant trials GALVALUME coils were post-treated with organic chromate solutions exhibiting different Cr-contents. The corrosion behaviour was observed by visual evaluation of white rust (according to DIN 53210) on flat panels after exposure in a humidity cabinet according to DIN 50017; preliminary results are shown in Fig.1. Obviously even relatively low Cr-contents retard formation of white rust significantly: on bare GALVALUME first white rust was observed after two cycles whereas on post-treated GALVALUME (Cr-content: $8,1 \text{ mg/m}^2$) only after 56 cycles which agrees well with the findings of other studies (4). Furthermore, the results reveal that even lower Cr-contents (less than 5 mg/m²) are sufficient to provide an effective temporary corrosion protection.

XVIII-2



Fig. 1. Post-treatment of GALVALUME with organic chromate solutions: Influence of Cr-content on formation of white rust.

CORROSION BEHAVIOUR OF PREPAINTED GALFAN

GALFAN samples with different coating thicknesses (7, 10, 14 and 19 µm each side) and painted with a two-layer system (chromate pretreatment, primer, white SP top-coat) were subjected to longterm atmospheric corrosion at different test sites representing rural, industrial and marine environments. For comparison samples of hot-dip galvanized steel sheet (Z) with similar coating thicknesses and paintings were also tested. Results of visual evaluation of red rust formation after 5 years are shown in Fig.2 indicating that flat and formed GALFAN as well has superior corrosion resistance compared to Z with comparable coating thicknesses. This is particularly obvious for samples exposed in marine environments. The relatively high corrosion rates in rural and industrial environment (particularly for formed panels) may be due to a very high wetness of the climate and temporarily high SO₂-concentrations in the atmosphere, respectively. Under such conditions differences in corrosion behaviour of GALFAN and Z are less significant.

The data presented in Fig.3 indicate that paint delamination at scribes down to the steel substrate on GALFAN is significantly less marked as compared to Z, independently of the atmosphere. The reason of GALFAN being favourable compared to Z may be due to higher sacrificial effect of the Z coating leading to locally accelerated dissolution of zinc and thus to more marked paint delaminations.



Fig. 2. Evaluation of red rust formation on prepainted GALFAN (ZA) and hot-dip galvanized steel sheet (Z) subjected to long-term atmospheric corrosion; thicknesses of the metallic coatings: 19 μm, painting: two coat system (white polyester topcoat). a) unformed panel, b) OT-bend



Fig. 3. Long-term atmospheric corrosion of GALFAN (ZA) and Z: Paint delamination at scribes down to the steel substrate.

CONCLUSIONS

It could be demonstrated that a **post-treatment** of GALVALUME with an organic chromate solution leads to significant improvement of corrosion resistance as compared to bare GALVALUME; first results on long-term atmospheric corrosion testing of **prepainted** GALFAN indicate a higher corrosion resistance and a significantly less marked paint delamination at scribes down to the steel substrate as compared to Z with similar coating thicknesses.

REFERENCES

- 1. L. Allegra, R.J. Dutton, A. Humayun Metalloberfläche 40, 329 (1986)
- 2. S.A. Kriner, K. Niederstein Bleche, Rohre, Profile 39, 109 (1992)
- 3. C. Filthaut ECCA Conference Transcript, Nov. 1991, Bruxelles
- 4. J. Sander, R. Mady Metalloberfläche 43, 329 (1989)



XVIII-6

I will report on what's happening in North America with the development of Galant. It's no secret that there are some well-entrenched zinc products in North America regular galvanized (both hot-dipped and EG) and Galvalume are very well established in North America and until the time that we have multiple Galfan producers in North America, Galfan cannot grow very large, it's going to stay small. We are already starting to see results from the second sheet producer (Wheeling-Pittsburgh) coming on stream.

With multiple wire producers now on the horizon and about five tube coaters, the market is going to start growing. I don't know how many of you ever looked at the growth of Galvalume, but after Bethlehem Steel invented the product, for about five or six years it just bounced along because there was only one producer. Then National Steel, which I happened to be with at the time, was the second company to get into Galvalume. I did a lot of work with Galvalume and very shortly after that LTV, US Steel and many other companies came on board and the product had a dramatic growth rate which hasn't stopped yet. I think we will see something very similar in Galfan. Look at the experience in Japan with multiple producers; and now Europe with multiple producers you can see that same kind of growth.

The North American Galfan® Development Association was basically established to promote Galfan in North America. We wrestled for a name and came up with The North American Galfan Development Association using the acronym of NAGDA. We are now a little bit over a year old. Galfan producers of course support this organization including: Sheet Producers, Wire Producers, Tubing Producers. We have had even better support from the Galfan Alloy Suppliers and zinc suppliers. Then there is a very important group of suppliers to the producers who are a part of the organization and truly help to support it. I want to take a minute to say that many of the suppliers are here in this room. We truly thank you for that support because its very helpful in this total development. and we are very appreciative of that. We set up the association, we had bylaws written, and we have a board of directors. We could hold a board meeting here because Tom Ranck, John Hostetler, John Malmgreen, Dave Parrish and I are all on the board — we are missing only two board members.

During 1992, we had two regular meetings of the total association and just so you can get an appreciation would the members of the association just raise their hands that are here so you'll get the see, because a lot of the suppliers and associate members are here. You'll get to see there is a good cross section of membership in the association. The most recent meeting was held in Pittsburgh last week with 34 people present at that meeting, the highest turnout that we have had.

What are we doing? We've established some committees. The first one is membership. John Hostetler happens to be chairman of that committee. When the association was established, we decided that membership should be for active Galfan producers in North America or active licensees whose primary business transpires in North America or the associate members who are the supplier members whose business is in North America. A candidate for membership must be nominated by an existing regular member, then complete a membership application which goes to the membership committee for processing and who then bring it to the board for approval.

We now have two other sections. One is the marketing committee, headed up by Glen Nishimura of Noranda Zinc. The marketing committee has established some things that have been very effective. The first one is a speakers bureau. I don't know what it is like in Europe or in Japan when you go and speak to an organization as a member of a company like Weirton Steel or Sumitomo Metals, but a lot of times when you do that, you are seen as a salesman, but if you represent an association and speak for that association, you're seen not just as someone selling — you're seen as a representative or agent and perceived in a different light.

as more than Weirton Galfan — it's now more universal.

The speakers' bureau has prepared a slide presentation so that any member of the association can go out and speak to an audience about Galfan sheet, wire, or tubing applications — I am a sheet producer and I knew very little about wire and tubing, but now I can speak a little more comfortably about Galfan because of this presentation.

Promotion activities — we distributed articles that have been published in the U.S. on Galfan written by the association members. The editors like to get those kinds of articles. In two weeks in Chicago, is the International MetalCon Show which can include anything to do with the use of metal in construction. One of the education panels at that trade show is on steel substrates. There will be a presentation not only on galvanized, Galvalume, and Galfan but also on copper, tin, and a lot of other materials used in construction. But, I'll be representing NAGDA — and speaking on Galfan. It's a pleasure to do that because there will be large audience there — there are over 300 booths already sold at the trade show, so it's an excellent place to get the Galfan word out. People worldwide that have anything to do with construction will be there.

Publicity — we have an advertising agency to do publicity releases on Galfan that any of the members of the association want to release to the press. It's a very effective way, again, of getting out your message to the public. We also saw a need for some kind of technical development within the association. Again, with the purpose of the association to promote Galfan in North America, we looked at how to do that from a technical standpoint. We broke the technology section into two parts. The first is *process or operating-type* technolocy and Tom Ranck of Ferro Technologies chairs that committee. A lot of the work that his committee is working on is the cold flux line development for Galfan.

it is a key thing. We are looking at Galfah as an environmentally mendry product because of its very low lead content. With a pure Galfan bath you have no lead to get rid of, no antimony, no additives, none of the things that are going to be very difficult from the environmental standpoint in the future. So we are promoting Galfan now as an environmentally-friendly product, and the environment-sensitive customers consider that as a very important criteria in the future.

The technical *Product Development Committee* is to help sell the product in the marketplace. The chairman of that group is Bob Goodhart of Weirton Steel. One of the things this group is working on are specifications; very critical because everybody has to relate something to a specification. They will also develop performance sheets of selected Galfan applications that are accepted in the marketplace. ILZRO is committed to a lot of testing. One of the major projects right now in the U.S. will test Galfan performance in soil and concrete. Some work was already done in the past, but there was really not enough data to be useful and so ILZRO plans to continue it. The important thing is everything that this group will work on is directed from the marketing group who know where the payback will be in the marketplace. I think that's important to understand.

Basically, that's the end of my report. I'll be happy to answer any questions that anybody has.

<u>Chairman:</u> Your comment about the environment just jogged my memory. There is another consideration that really doesn't have anything to do with selling in the conventional way; that's the matter of recyclability. I have heard the comment that in the future many decisions as to what product will be used will not be based on whether its the best or second best or even the worst, but it is going to be based on whether the product can be recycled or not. That's a matter I think we need to consider, so I'm especially interested in finding someone who can present some hard information to our neip.

<u>Dubois:</u> I read the brochure you had presented and get the feeling that you try to promote only bare Galfan.

<u>Celestin</u>: No that's not true. The brochure was a low budget project so we couldn't put a lot of color in it. There's no question in my mind that Galfan should be painted because that is the market Weirton is emphasizing, but we are also after deep drawn unpainted applications. We tried to cover everything in this brochure.

<u>Chairman</u>: I think a lot of it was just simply the difficulty to present a comprehensive story. It's pretty easy to talk about unpainted Galfan but because of the variety of paint systems and the applications, it is very difficult in a limited amount of time and space, and this literature project was a very short-time project.

Another benefit of NAGDA is that it provides opportunity for suppliers to educate the Galfan family of their products and services. I think an example was last week's NAGDA meeting where we did have a representative from Magni, the company that makes the paint used for topcoating Galfan automotive tubing. He had a chance to talk to all the Galfan Licensees at one time under ideal conditions. So that is certainly one of the uses of the association; it can bring people with a product or technical expertise to the entire audience and make it worth his while.

Just because the first application was for tubing, doesn't mean that you cannot apply it to wire or sheet. In fact, there is strong evidence to indicate the Al-rich topcoat used for tubing will also do well on Galfan sheet as fuel tank material.

•

the history of discussion to organize cooperative European Galfan Market Development, it is useful to mention that three first steps made up till now. Initiated by ILZRO, the first meeting to discuss this subject was held in October, 1991 in Pittsburgh during the last Galfan Meeting. After receiving interesting information about NAGDA presented by Mr. Celestin, I can say that the attendants agreed that something should be done for promoting Galfan in Europe.

A second formal meeting to discuss this subject was held in January, 1992 in Brussels. The conclusion of this meeting was that cooperative Galfan development in Europe is needed to promote general publicity and should be undertaken, but a volunteer structure is not sufficient for this effort. A separate organization or individual is needed to carry out the work.

As a result of the conclusions of this meeting, ILZRO formally solicited for proposals. The European Galfan Licensees were asked to respond to this proposal. Answers were received from candidates in the United Kingdom, Belgium, and Germany. The English proposal mentioned that the funding suggested should be spent on the production of a brochure which would be designed for targets specified by the European Galfan producers. A 24-hour answering telephone would also be available for helping potential customers or users in a Galfan office. It was noted that the Belgian offer proposed to stimulate both demand and supply because he felt that merely to stimulate demand is not enough. The proposal also noted the need to work together with producer for filing companies — often subsidiaries of the first, architects, metal engineering firms, and large contractors to bring Galfan to a fully commercial position across Europe.

Considering that the construction market is the most important, it will be important to focus on manufacturers of profiled and color coated products. This consultant's proposal mostly relies on his personal contacts to stimulate Galfan demand but would

other markets would be addressed.

The three proposals were discussed during the third meeting held in September, 1992 in Amsterdam. It finally appeared that no proposal fully satisfied the attendees. If a development effort was carried out, it was needed to put more dynamics into it. It was suggested to form a small group of marketing experts, elected by the sponsors who finance the work, to steer the effort. By this way it was then possible to integrate the opinions of the many producers and to chose an independent marketing professional for organizing and managing the effort.

The steering committee could be helpful in identifying the direction and in contacting the coil coaters and steel producers. The Galfan Development person should be very dynamic and should serve as a catalyst to work with Galfan producers. It was urged that further development of the Belgian and German proposal be undertaken in accordance with the sentiments of the committee. The proposers would be asked to provide more details in their proposal to address the approaches and attitude along with the agreement toward working with the steering committee.

After receiving revised proposals they would be mailed out to the entire group of European Galfan Licensees. The formal meeting to begin this effort was anticipated for January, 1992.

So gentlemen, I hope you have summarized the first steps which will lead in the near future to the European Galfan Development Association.

Thank you for your kind attention.

<u>Hostetler</u>: One of the immediate differences between the two organizations appears to be that the European group feels that it will take the efforts of at least one full-time person to carry out what the association wants to accomplish. The North American

opinions and all the policies of these companies.

<u>Hostetler</u>: I think North America has the advantage of starting while the program is still very young and not a lot of things to bring along or to orchestrate and coordinate, but I personally think that the North American group will also have to consider something beyond volunteer help before long.

<u>Leroy:</u> Is the French delegation not active in your group? <u>Pelini</u>: There are present but they have not made a proposal.

<u>Hostetler</u>: So, if I understand correctly what appears to be the proposal you're going to be considering now is for DVV to manage the operation but with the employment of someone who will be executing or working the program.

<u>Pelini:</u> Not exactly DVV. I think as you have heard there are two independent proposals. It is up to each one to explain how he can do the job and work with the steering committee. That is what must happen next.

Hostetler: When do you expect that the decision will be made.

<u>Pelini:</u> I think the effort will start in beginning of 1993. We have the next meeting anticipated for January and hope to start at this moment. The first step is to elect the steering committee.

<u>Williams</u>: It a general question which would apply both to European and to the North American associations. My concern is that most of the Galfan production appears to be going in as substitute for conventional zinc. What efforts are being made to survey and look for alternative products for Galfan so that we could increase the total output of coated products and not just substitute one for the other. or something else other than galvanized, so we have not experienced that.

Williams: I notice yesterday that the paper that John Hostetler presented on behalf of Hoesch, 50% of their output was going into prepaint and one can assume that that is straight replacement for zinc coatings products that were being used in that application previously. So my concern is that we actively pursue replacement for asbestos cement and other types of products so that we can increase the total output of the coated product.

Hostetler: I don't think that is any question but what much of the Galfan in the future is going to replace regular zinc coatings because it offers greater life, greater ductility, greater paintability. I don't think there is any question about that. At the same time, however, there is and needs to be an effort to seek these applications out where for the virtues of Galfan a steel product can now be made more corrosion resistant that is not presently galvanized or in other ways protected. The thing I thought maybe Mr. Celestin was going to present was the order for the post boxes, the kind that you see on the sidewalk where you dropped your mail in North America. Past attempts at galvanizing the roll-formed shape that supports that box simply could not produce good enough results for it to become a galvanized product, but with the advent of Galfan, the additional formability allows that product to be made without cracking and now with Galfan protection and post-painting, it will last maybe 15 years instead of 7 years. That's a product that now uses zinc that was not using zinc before. Not steel, but one that certainly is going to be protected. The interest of steel in that application. It wouldn't take much to envision that box being made out of aluminum, plastic, or some other material.

I do think that as we talk about where we're going to get the business for Galfan, we need to keep both in mind. I think legitimately, we must improve the performance of galvanized products. Galfan is a way to do that. Secondly, there are many applications
my interest is of course to find better ways of using Galfan and I know some of those are going to replace one or more of the other G's, no question about it.

<u>Dewitte</u>: In the wire business there are already applications that were using stainless steel and now use Galfan coated wire and there you take advantage of the strength of the steel and if the coating can give you enough protection from corrosion, then you have an opportunity to replace the stainless steel product to the customer.

<u>Capul</u>: I don't know how well we'll be able to slug it out with stainless, but certainly in our country with cadmium plating being very environmentally bad, I think we can slug it out very favorably with anybody that's plating cad.

<u>Hostetler:</u> I ran across an application in Czechoslovakia a couple of weeks ago where they are making noise abatement panels using a very light gauge picture frame on steel. The back panel which is about three-fourths of the weight is some kind of a composition board. Its got gypsum and a couple of other products in it. The front is perforated aluminum and of course a blanket of fiberglass on the inside. That whole thing should be made from prepainted Galfan coated steel. Properly engineered and designed, I think that product could be converted to prepainted Galfan coated steel. XX-6