SEVENTH GALFAN LICENSEES MEETING

Technical Meeting

December 5, 1985

INTERNATIONAL LEAD ZINC RESEARCH ORGANIZATION, INC.

MINUTES OF THE GALFAN LICENSEES TECHNICAL MEETING

Held At

Hotel Metropole
Brussels, Belgium

On

December 5, 1985

ATTENDANCE

| NAME | COMPANY |
|---|---|
| U. Brill | Thyssen Stahl Ag |
| P. Bourgeois | Galvameuse |
| J.P. Branciaroli | Mineral Research & Development Co. |
| J. Brugarolas | Procoat |
| E. Buscarlet | Ziegler S.A. |
| A. Celestin | Weirton Steel Corp. |
| R. Celis | Fils et Cables D,Acier de Lens |
| H. Chatami | Kawasaki Steel Corporation |
| D. Coutsouradis | CRM |
| J.R. Crampton | Laporte Industries, Ltd. (Mineral Research & Development Group) |
| M. Dam | ECCA, Brussels |
| A. Davin | CRM |
| M. Dewitte | Bekaert |
| G. Durand | Fabrique de Fer de Maubeuge |
| H.P. Ferret | FICAL |
| F.E. Goodwin | ILZRO |
| C.W. Haines | AM&S Europe, Ltd. |
| Y. Hirose | Nisshin Steel |
| D. Jones | British Steel |
| T. Jore | Norzink As |
| I. Kamimura | Nisshin Steel |
| J. Kiyasu | Kawasaki Steel Corporation |
| P.A. Lakerveld | Billiton Zink B.V. Holland |
| J. Lamesch | Arbed |
| A. Matthews | British Steel Corporation |
| A. Nikoleizig | Thyssen Stahl Ag |
| J.L. Pagniez | CITAG |
| C. Parma | Cotimpi Snc. |
| J. Pelerin | Phenix Works |
| P. Pichant | Usinor |
| P. Piessen | Centre Technique du Zinc |
| V. Rispoli | Cantieri Metallurgici Italiani |

| NAME | COMPANY |
|---|---|
| C.E. Roberts | ILZRO |
| I. Robertson | Noranda (London) |
| D. Rollez | MHO |
| F. Sanguigno | Cantieri Metallurgici Italiani |
| W. Schwarz | Hoesch Stahl Ag |
| Y. Shimada | Sumitomo Metal |
| A. Skenazi | CRM |
| J.A. Southern | AM&S Europe, Ltd. |
| I. Toomer | Zinctek (Palmer Tube Mills) |
| F. Verhoeven | Bekaert |
| H. Wagener | Arbed S.A. |
| R. Zwingmann | Hoesch Stahl Ag |

Dr F.E. Goodwin served as Chairman and also took the minutes.

## MEETING CONVENED

The meeting was convened at 9:35 a.m. by Dr. Goodwin who welcomed all attendees to this Seventh GALFAN Licensees Meeting. He gave a special welcome to the ILZRO members who were present and noted that their continued sponsorship of the CRM GALFAN research made much of the future progress and GALFAN characterization possible. He also welcomed the various suppliers who were present and thanked them for their partial sponsorship of this series of meetings. He noted that the technical session of these meetings is regarded as being a closed meeting and thus information should not be published out of the proceedings of these meetings without checking first with ILZRO as to the status of its confidentiality. There have been several reports in the past year which have used such information, he noted, and future work should be checked for clearance. He then asked each of the attendees present to introduce themselves to the rest of the group. Following this, an attendance roster was circulated.

## REPORT ON CRM RESEARCH

Mr. Skenazi presented the research results of CRM and noted that the report was divided into three sections. First, the most recent corrosion data, second, the development of a single-dip wire galvanizing process and third, other 1985 research activities at CRM.

### Corrosion Research Report

Mr. Skenazi began by reviewing the past results on salt spray testing of GALFAN and galvanized and the long-term exposure results of two-years duration on commercial quality material. He noted that the one-year results showed very little weight loss difference between various coatings on this exposure program. After two years, however, significant differences in weight loss were seen in marine, severe marine and industrial exposures. Not much difference was seen for examples exposed in the rural environment. A bar graph shown previously gave the results after one and two years. Also, the previous work on the effect of chromating and structure on the GALFAN corrosion rate was reviewed. Microstructures examined after two years of exposure were also described to the group. All of the samples exhibited some form of local corrosion after two years of long-term exposure on the various sites.

A new long-term exposure program was begun during 1984 at CRM. One-year exposure data are now available from the industrial site. It is planned to continue this exposure program up to 15 years. One advantage of this program is that it uses samples of 200 x 150 millimeter size compared to the most smaller, older samples. This should eliminate some of the edge effects which were seen with the older samples. Mr. Skenazi noted the corrosion data which has appeared in the literature from many sources. Regular zinc galvanizing coatings are compared with various zinc near 5%-aluminum alloy coatings such as Superzinc, GALFAN and the Bethlehem Steel pilot line coating. The ratio of corrosion rates of the alloy coatings to the normal galvanized coatings was shown for the various investigations. They ranged from 1.03 up 1.55. The material exposed in the atmosphere at Liege from October, 1984 to October, 1985 was characterized and showed that galvanized corrodes two times as fast as GALFAN, and GALFAN corrodes two times as fast as Galvalume in this environment.

As part of this work, a multi-level factorial analysis was set up to determine the effect of the various GALFAN coating details on corrosion rates. The effect of coating structure, that is regular or eutectic, was examined along with the presence of absence of temper rolling, chromating, and heavy or light gauge substrate. It was found that the thickness of the steel had the greatest effect upon corrosion rate giving a contribution of 0.6 microns out of the 2 microns per year corrosion rate in Liege. The structure type gave the next largest contribution, resulting in a 0.4 micron difference in corrosion rates. The eutectic structure had the higher corrosion resistance. Skin-passing had a relatively low effect on corrosion rate. 0.1 micron improvements in corrosion resistance were seen with skin-passed materials. Finally, chromating gave a .2 micron difference in corrosion rates, with the chromated material showing the better corrosion resistance. Mr. Skenazi cautioned that this material could only be used to interpret one-year corrosion results, as longer term results would probably have different kinetics involved. However, it could seen that a minimum corrosion rate of 0.7 microns per year was obtainable with GALFAN having optimum processing. The worst material examined had a corrosion rate of 2 microns per year.

To determine the rate of darkening on GALFAN, galvanized and Galvalume under chromated and non-chromated conditions, light reflectance measurements were taken using a light meter across the entire light spectrum. Unchromated GALFAN had a reflectance of 40% before one-year industrial exposure and 25% afterwards. Chromated GALFAN had a reflectance of 50% before exposure and 35% afterwards. Chromated galvanized had a reflectance of 50% before exposure and 35% afterwards. Unchromated galvalume had a reflectance of 90% before exposure and 60% after. Thus, chromated GALFAN and galvanized have the same performance, unchromated GALFAN has the worst and unchromated galvalume has the best. Dr. Hirose asked about the combined defects of chromating and temper rolling on the corrosion resistance of GALFAN. He asked if chromium was applied to the sheet before or after skin-passing. It was determined from the group that chromates were generally applied after skin-pass, and that this was the case for the samples involved. Mr. Lamesch noted that the reflectivity results for Aluzinc were correct but the chromated Aluzinc is more commonly used when reflectivity is required. He proposed that this be included in the program. Mr. Skenazi noted that no chromated Aluzinc was available at the time of this work, however, it should be sent to CRM so that it could be included in the program. Mr. Lamesch and Mr. Skenazi agreed that the thickness and weight loss measurements between coatings can be misleading depending upon the measurement techniques used and the purpose of the experiment. Dr. Goodwin asked CRM to include the thickness in weight loss calculation techniques in the next GALFAN Progress Report for GALFAN and Galvalume. Mr. Haines asked what the reason was for the poorer corrosion performance of GALFAN when the thick gauge material was used. Mr. Skenazi replied that this was due to rusting of the steel away from the edges where the coating was located and also due to a higher depletion of coating at those areas because of a greater requirement for galvanic protection. Mr. Nickeleizig asked if any results were obtained on formed parts during this investigation. Mr. Skenazi replied that no quantitative data is available, only percent red rust on samples has been obtained. Mr. Hirose noted that the chromate levels on GALFAN, galvanized and Galvalume do differ considerably and asked if this had been accounted for in the sensitivity analysis done by CRM. Mr. Skenazi noted that the factorial analysis had only considered GALFAN and that no attempt was made to compare the effect of chromating on the factorial level analysis to Galvalume and galvanized. He noted that the chromate levels do differ between the various coatings. Mr. Pelerin noted that pilot line material from the early CRM investigations has been exposed since 1980 at CRM. He asked about the results from these materials. Mr. Skenazi noted that CRM continues to expose these old panels but that the panels are so small that strong edge effects are noted which affect the corrosion results quite strongly. Thus, they are not entirely suitable for quantitative corrosion results. However, he noted that in the severe marine atmosphere, the galvanized coating has a 20 micron coating which shows severe red rust. Here, the GALFAN coating with a 20 micron coating remains intact with a small amount of red rust. Mr. Skenazi also noted that it is impossible to do quantitative analysis on samples with a lot of red rust.

Mr. Skenazi reviewed the latest results on soil burial corrosion in clay soil. He first reviewed the results on one-year exposure which had been shown last year on GALFAN, galvanized, Galvalume and aluminized steels. The samples had been again dug up after two years of exposure and were shown to the group. The samples were both chromated and unchromated and have varying radius bends along with an impact bulge. Pitting is seen on all samples, however, little red rust is seen on the galvanized and GALFAN samples. Severe red rust is seen on the Galvalume and aluminized samples when the coating is pitted. Also, the edges of the Galvalume and aluminized samples are heavily rusted.

Formability Testing

Mr. Skenazi noted that CRM had previously done forming limit diagrams for galvanized and GALFAN. The effect of forming on salt spray behavior had been determined. New data was shown for limiting dome height tests. These used drawing quality steel for both coatings and an equivalent coating weight. It showed that the GALFAN samples had a slightly higher limiting dome height than the galvanized panels. Corrosion resistance tests will be carried out on the samples.

Relating to this work, CRM has compiled the undervehicle testing from its work in Liege during the last few years. It will published for the sponsoring members, and will made generally available during 1986. Mr. Skenazi then summarized the GALFAN properties which had evolved from this work. Compared to galvanized, it has improved corrosion resistance and equivalent cathodic protection. It has far better ductility than most other coatings and an ease of processing equivalent to normal galvanized. Its welding characteristics are good, its painting characteristics are excellent, and it is a fully commercial product in several regions of the world.

Mr. Hirose asked how the pitting sensitivity of GALFAN in the clay soil was. Mr. Skenazi noted that some pitting sensitivity is seen in the older material but not so much in the latest material.

## WIRE RESEARCH

Mr. Skenazi reviewed the problems in developing a GALFAN compatible flux. This problem had been avoided by developing a double-dip wire GALFAN coated process. This process is now fully commercial. Single-dip wire coating of GALFAN required testing of many fluxes and culminated in commercial pilot work at the plant of Technoarbed in Luxemburg. During the first trials, the single-dip coating process did not produce consistently good quality material. An alternative was to use a zinc electrocoating pretreatment, however, this resulted in technical and economic drawbacks. At least 10 microns of zinc electroplate on the wire was needed to get a GALFAN coating of accessible quality on top of this pretreatment. Because the GALFAN alloy has a lower reactivity with steel, there have been problems in preparing steel wire to take a good GALFAN coating. The approach taken at CRM was to use a meniscograph to examine wetting characteristics of various fluxes in combination with GALFAN.

The meniscograph looks at the change of weight of the samples due to the meniscus affect. Different fluxes and bath compositions were examined during this work. Ammonium chloride improves the wetting force of flux when the composition of the ammonium chloride exceeds 6%. This is shown in an attached graph. Some error results in this work because of a build-up of flux residues which hang on to the strip and bring up the weight of the sample. The wettability can also be affected by wetting agents. Overall, it was found that problems of bare spots and uncoated areas were due to insufficient pickling of the wire. Black spots and rough spots were due to too much or too little reactivity on the part of the fluxes. A quality index from one to ten was devised to rate samples produced during the work. Temperature also has an effect on flux wettability. There is an optimum range for high wetting forces. Wettability of the flux is also affected by iron contamination. There is a higher tolerance to iron at higher bath temperatures. Behavior of two fluxes in the GALFAN bath were examined. The meniscograph charts for these two fluxes are shown in an attached graph.

Mr. Skenazi then described corrosion testing which had then been done on both single-dip and double-dip wire. Some differences were expected because of the difference in structure of the single-dip and double-dip wires. The single-dip wire has a very slight or non-existent intermetallic, whereas the double-dip wire has quite a thick intermetallic layer. There is also a difference in coating weights between the two products. A problem of lead contamination was also seen in production of the double-dip wire. Single-dip wire seemed less sensitive to intergranular corrosion than the double-dip wire. However, both types of products gave two to three times the corrosion resistance of normal galvanized wire in salt spray results. Photographs of wire after kesternich testing was shown. Twelve (12) cycles of testing were used to produce the results. Both single-dip and double-dip wires can do well under certain manufacturing conditions. Bright samples of both single-dip and double-dip wire were shown, however, under other manufacturing conditions the twelve cycle kesternich test gave brown wires. Work at CRM has also carried out quantitative corrosion testing of galvanized and GALFAN wire using the 3PPM sulfur dioxide test. It was found that galvanized wire corrodes at a rate of 6 microns per week, whereas GALFAN corrodes at a rate of 2 microns per week. The samples were not dissolved down to the intermetallic layer so it cannot be yet determined if the intermetallic layer has an affect on corrosion rate. CRM will begin a more extensive wire corrosion testprogram when a variety of wires from various producers are available for testing.

A description of the testing done of single-dip wire is attached to these minutes.

Mr. Durand asked what the range of temperature given the optimum wetting force with the fluxes was found to be. Mr. Skenazi replied that the GALFAN bath temperature was found to be good for this between 400 and 460 degrees C. Mr. Hirose asked what the applicability to Cook Nortemann sheet lines would be. Mr. Skenazi replied that it should be generally applicable. However, cleanliness is critical when preparing material for coating.

PHENIX WORKS

Mr. Pelerin described the work that Phenix Works had done over the last year on the effect of cooling rate on the GALFAN microstructure and the effect of the GALFAN microstructure on corrosion of coil coated material. He stated that during their trials and through investigation of material provided by other licensees, it had been concluded that the zinc rich phase of the GALFAN coating was suppressed by more rapidly cooling the material. He believes that this structure has an influence on coating performance. He reviewed the CRM cooling rate study which had taken place several years ago. This study had looked at cooling rates of the GALFAN coating from 2 degrees C per second up to several hundred degrees C per second. He noted that most galvanizing lines have cooling capabilities of slow cooling up to about 40 degrees C per second. Various lines have special arrangements to get much higher cooling rates. After the campaign of Phenix Works in 1984, a program on the effect of cooling rate on corrosion resistance of coil coated product was begun. Regarding their coil coating line, the only modification was an adaptation of the degreasing section.

Characterization of the coil coated material showed that good adherence was obtained compared to hot-dip galvanized coil coated material. Some edge creep on the GALFAN coatings with salt spray test was found and the object of the investigation was to determine if cooling rate affects this. Coils from Ziegler and Phenix campaigns were coil coated at Phenix Works. Mr. Pelerin described the characteristics of these coils which had varying cooling rates and in some cases were skin-passed or chromated. A variety of coating weights was also used. The coil coating process at Phenix consisted of a Parcolene 338 cleaner, a Bonderite 1303 pretreatment, an epoxy primer, and either a silicone polyester or a PVC plastisol topcoat. Tests used to characterize these samples were mechanical deformation by T-bends and impact, corrosion is salt spray from which edge creep after 750 and 1,000 hours was taken, and long-term corrosion exposure. No microcracking was seen on the panels after mechanical deformation. The only problems were seen with samples which had very high cooling rates, that is around 200 degrees C per second. Problems were seen with the coating integrity at these high cooling rates. The intermediate cooling rates, around 30 or 40 degrees C per second gave the best results. The corrosion performance of coil coated GALFAN in salt spray was very good compared to galvanized. Far less edge creep was seen with the GALFAN panels. Also, much less microcracking was seen with the GALFAN coil coated panels compared with galvanized after salt spray. Mr. Pelerin noted that the very high cooling rate panels had microcracking problems.

Mr. Pelerin also showed photos of samples coil coated with the two paint systems noted above after two years of exposure in marine, severe marine, industrial, and rural environments. In contrast to the salt spray tests, no edge creep at all was seen on the GALFAN panels after the two years of exposure. Thus, the edge creep seen in salt spray tests is not confirmed by this testing.

Mr. Matthews asked if Mr. Pelerin knew what the effect of Heurtey minimization would be on coil coating performance compared to cooling. Mr. Pelerin replied that the most important thing was to have as homogeneous a structure as possible. The Heurtey minimization process should help this and he saw no problem in coil coating this material. Mr. Skenazi noted that fast cooled Ziegler material was being held on long-term exposure racks as part of the CRM program. Corrosion results would be available on this material on the next Licensees Meeting. Mr. Lamesch asked what the typical ranges of cooling rates used at Phenix Works was. Mr. Pelerin replied that it was 30 to 40 degrees C per second for fast cooling.

Mr. Buscarlet noted that Ziegler has not looked at the problem of the effect of cooling rate on coil coated performance. They have put prepainted GALFAN out on exposure at Irsid. Good results have been obtained on this product, however, fast cooled material (around 200 degrees per second cooling) has not been included with this material. Mr. Southern asked how GALFAN compared with other substrates with regard to edge corrosion. Mr. Pelerin replied that either GALFAN or Galvalume substrates perform better than a galvanized substrate for coil coating. Mr. Southern noted that Australian work being carried out noted that the coil coating performance of GALFAN substrates is superb. Mr. Buscarlet agreed with this and noted that the GALFAN samples on exposure at Irsid with polyester paint had shown superior performance over normal galvanized. Mr. Coutsouradis asked if the two-year exposure was a long enough time to be convincing. Mr. Pelerin replied that three years should be even more convincing and should certainly correlate well with the two-year results. Mr. Robertson asked how the performance of unpainted fast cooled GALFAN would be if microcracking was a problem. Mr. Pelerin replied that microcracks should not be a problem in fast cooled GALFAN because of the sacrificial protection which was available. Mr. Robertson asked if the skin-pass over the microcrack material would cause a temporary flattening which could reopen under corrosion conditions. Mr. Pelerin replied he didn't think this was likely. Mr. Jones agreed that temper rolling does not affect microcracking on GALFAN. GALFAN is more flexible than galvanized in any event and is not as sensitive to cracking. Mr. Matthews noted that there was a great need in the market place for a GALFAN product with a single pedigree. He asked the licensees if they should consider selling only one product with a predictable performance. This would be much better for the consumer thanto sell a lot of different GALFAN products which have different microstructures.

NISSHIN STEEL

Mr. Hirose presented a paper on the effect the varying aluminum concentration on the performance of GALFAN. A copy of his report is enclosed with these minutes. Mr. Hirose reviewed the early work by Zoccola of Bethlehem Steel, which showed the effect of aluminum concentration in the coating on weight loss at various long-term exposure sites. He believed that the data was not as sharply dependent on aluminum concentration as this data showed. He had looked at three aluminum concentrations at 4, 5 and 7 percent for this work. Microstructures are shown in a figure in his report. The 4% aluminum microstructure features a zinc rich phase, whereas the 5% phase is entirely the eutectic structure and the aluminum rich phase is predominant at the 7% aluminum level. The transmission electron micrograph is shown for samples which were cooled at 5 and 30 degrees C per second. Further analysis of the primary particles present in the structure shows that some aluminum is dissolved in the zinc primary phase. Mr. Hirose also explained the aluminum concentration on the grain boundary depression which is seen in slowly cooled GALFAN coatings. A microstructure and the relationship between aluminum concentration and grain boundary dent angle are shown in the figures attached to these minutes. He noted that the time to red rust was either the 4, 5 or 7 percent aluminum alloys are all approximately the same. However, the weight loss due to white rust of the 4 and 7 percent alloy is lower than the 5 percent alloy. The effect of cooling rate on microstructure and the effect of magnesium on salt spray resistance of the 4% aluminum alloy was described. Magnesium is an important component in the Nippon Steel Superzinc alloy and is of interest to this work. Some of effect of cooling rate on salt spray corrosion resistance was seen. Ductility of coatings was checked by a 2T bend. No difference with aluminum composition was seen. A deep drawn cup was made and salt sprayed for 500 hours with several different aluminum compositions. Similar behavior was seen. The effect of aluminum on the percentage build-up of aluminum in the phosphate pretreatment solution for coil coating was observed to be strong with increasing aluminum composition. A chart of this relationship is also shown. Mr. Hirose concluded that there is no big difference in the performance of 4, 5 or 7 percent aluminum composition. However, phosphate build-up of aluminum contamination is a problem with coil coating lines. The grain boundary dent at the 5% composition is also observed to be larger than at other compositions with the cooling rates used. He urged that the group set a composition standard with these ideas in mind. He proposed that a lower limit of 3.7% aluminum be set instead of the standing 4.7% aluminum figure.

Dr. Goodwin asked what the percent mischmetal was in the coatings that were examined. Mr. Hirose replied that mischmetal, according to this specification, was added to all coatings. Mr. Skenazi noted that CRM had not found the grain boundary dents in any of the samples that were seen and asked if it might be due to the coating thickness examined. Mr. Hirose replied that it was found for all coating thicknesses and indeed he found grain boundary dents in the Ziegler samples which were obtained from the first Ziegler trial. Dr. Goodwin asked about the effect of cooling rate on the grain boundary dents and noted that it was probably lessened with higher cooling rate because of the dependence upon cooling rate of the corrosion resistance as shown in this paper. Mr. Robertson asked about the micrograph shown on Mr. Hirose's figures of the grain boundary dent, and asked if this wasn't a worse case phenomenon.

Mr. Southern noted that the grain boundary dent problem was common with lead containing galvanized alloys, however, it was not a serious problem. Mr. Hirose replied that lead containing galvanized does not present a problem for Nisshin Steel when it is unpainted but it does present a problem for prepainted material. Dr. Goodwin noted that the problems of coil coating of lead containing galvanized were related to segregation of the lead in the coating rather than a problem of grain boundary dent. Mr. Hirose agreed with this. Mr. Buscarlet asked what line speed was used on Nisshin's pilot line which was used to prepare this material. Mr. Hirose replied that a speed of 15 meters per minute was used. Mr. Buscarlet noted that under these conditions using the minimizing device, the coarseness of the structure was suspect. He thought it was too big for the cooling rate shown.

A slide of the grain boundary dent was again shown to the group. Mr. Pelerin noted that he had seen similar phenomena on the Yodogawa material which was examined during 1983. Some pulling away of the coating at the grain boundaries by the primary zinc particle was evident. The group was unresolved on the question of the seriousness of the grain boundary dent problem.

## HOESCH STAHL

Mr. Zwingmann reviewed the production of GALFAN which had taken place recently on their line in Eichen. A copy of his remarks are attached to these minutes. Mr. Zwingmann noted that very little cerium and lanthanum is found in the coating compared to the ingots which are put into the bath. Cooling is carried out by used vaporized water or air.

Mr. Dewitte asked why the lead concentration was higher in the coating than in the bath. Mr. Zwingmann replied that he did not know why this occurred but it must come from the pumping of the system when the zinc bath is interchanged with the GALFAN bath. Mr. Durand asked why crystals of zinc formed on top of the fast-cooled material but not on the bottom of the thick gauge. Mr. Zwingmann noted that this had to do with the discussion of crystallization which is found in his paper but the answer in not really known. Mr. Coutsouradis asked about the effect of line speed on coating thickness and ripple effects. Mr. Zwingmann replied that these had little effect and that the effect of air pressure on the ripples was the biggest problem. He also noted that this was not a problem for production of normal galvanized steel.

FABRIQUE DE FER DE MAUBEUGE

Mr. Durand reported on his company's recent production experience. A summary of his comments is attached to these minutes. He noted that to date Maubeuge has made more than 20,000 tons of GALFAN-coated strip. Because the GALFAN-coated strip is very bright, the quality of the strip is of extreme importance. The reflectivity of the strip allows for defects to be seen clearly. They had traced the main cause of bare spots to the practice of using the annealing furnace for galvanizing. Uncovered areas are mostly related to problems in controlling the air knives. This is particularly a problem when using light coatings. Finally, a problem with coating integrity due to entrapment of bottom drops had been discovered. More information is needed on this. The parameters of Maubeuge galvanizing campaigns is attached to these minutes.

Maubeuge had also carried out corrosion testing of GALFAN and galvanized steels in acidic and basic soils. Corrosion evaluation was done by comparing weight loss of each of the samples. GALFAN showed superior performance in all cases. GALFAN performed particularly well in a basic soil.

They are finding a good application for GALFAN in sheet using low coating weights. Here the market requires a very good surface which is not a problem for them. They are producing uniform coatings with a high smoothness. For the painted market, a medium coating weight is desired. For a coating weight of 225 grams per square meter, the standard 5% red rust salt spray test gives 400 hours for unpainted hours and 2,000 hours for painted GALFAN. For premium painted markets and embossed plastisol paint is sold. Samples of this were shown to the group. Mr.Durand noted that samples tested with an Erichsen bulge in a 4-hour boiling water test gave very good results. Thus, they believe GALFAN is suitable to a wide variety of applications.

Mr. Matthews asked about the accumulations of cerium and lanthanum in the dross of the pot at Hoesch and Maubeuge. He asked Mr. Zwingmann if the pumping operating at Hoesch cause any depletion of the cerium and lanthanum. He thought this would be particularly a problem because Hoesch makes ingots out of its GALFAN bath each time a campaign is run. Mr. Zwingmann replied that in their case, old ingot is mixed up with new ingot before each GALFAN campaign and, thus depletion is not that much of a problem. Mr. Durand noted that during the campaign of Maubeuge, mostly new ingot is used. Mr. Jones asked if Maubeuge had measured the thickness of the aluminum oxide layer on their nitrogen wiped GALFAN. Mr. Durand thought that the aluminum oxide layer would be thinner than that of air wiped GALFAN but that he believed it was present in all cases. It would not disappear completely, he believed.

KAWASAKI STEEL

Mr. Kiyasu presented a paper on the work Kawasaki had carried out to determine ways of determining uniform microstructure in GALFAN. A copy is attached to these minutes. The work found that uniform microstructures in GALFAN coatings can be obtained with a wide variety of immersion temperatures but that only low bath temperatures could be used to obtain uniformed coating structures. The bath temperature of 460 degrees C was the best bath temperature of those investigated. Cratering is a problem peculiar to the Japanese producers and it was found that cratering could be avoided with bath temperatures over 500 degrees C in this investigation. The work of Kawasaki also showed that corrosion in GALFAN occurs selectively between the eutectic and the aluminum rich primary phase.

Mr. Durand asked what the optimum process conditions would be based on the paper of Kawasaki. He noted that high bath temperatures were desirable for eliminating cratering but that low bath temperatures were desirable for microstructural uniformity. Mr. Matthews noted that if the optimum bath temperature is over 500 degrees C, then GALFAN cannot be used with the Zinquench process. Mr. Hirose asked what the eutectic composition was of the bath which Kawasaki used. Mr. Kiyasu noted that it was slightly in excess of 5 percent.

BRITISH STEEL

Mr. Jones noted that British Steel continues to evaluate GALFAN through its long-term corrosion tests on coil coated material. This is material which was produced during first Ziegler campaign and which had been coil coated by British Steel. Four years of exposure will be up soon, and 5 years of exposure will occur during 1986. At this time, a report on performance will be given to the group.

BEKAERT

Mr. Dewitte noted that Bekaert is continuing its research in development on GALFAN on a large scale. They hope to be ready for wire production commercially during June, 1986. They are looking for applications for GALFAN-coated wire in both high and low carbon wire product areas. A number of pilot campaigns have been made so far.

SUMITOMO STEEL

Mr. Shimada noted that Sumitomo planned to modify their #2 continuous galvanizing line at the Yakayama Steel Works. This will occur next spring. It will modify the main pot from a iron to a ceramic composition. Two separate sub pots will installed in addition to the main pot. Thus, several compositions can be changed easily in this galvanizing line. They plan to pump out the main pot to an empty subpot after which the full subpot containing another alloy will be premelted before this time and pumped into the main pot. Sumitomo anticipates having its first GALFAN campaign in May of 1986. Extensive lab tests have already been carried out which confirm the superior properties of GALFAN-coated steel.

ARBED

Mr. Lamesch noted that the activities at Techoarbed had been described during a CRM report to the group which is attached to these minutes. Their only activity is in the low carbon wire field. They began promoting this product several months ago in their markets and want to deliver tonnage soon.

INDUSTRIE CANTIERI METALLURGICI ITALIANA

Mr. Rispoli noted that CMI had taken a 2-month option on a GALFAN license and was studying conversion of their only galvanizing line in Naples at this time.

GALFAN PAINTABILITY

Cooperative Work in North America

Mr. Roberts reviewed the status of cooperative investigations which ILZRO is carrying out with various paint and pretreatment producers in North America. Studies at Parker and Heatbath have been concluded. Recent work at PPG, DuPont and Amchem are included in a progress report which was recently distributed to the licensees. Mr. Roberts reviewed the report within this document and noted that all investigators had found that GALFAN has performance in the coil coated condition which is at least equivalent to, or in many cases, superior to that of normal galvanized sheet.

Mr. Roberts also reported on the status of various independent investigations which were underway in North America. At the Ford Motor Company an automotive type paint system is being considered for evaluation. This is as a result of a very positive experience with stamping of GALFAN at the Chicago Heights, Illinois Stamping Plant of Ford Motor Company. The production people at this plant asked the Research & Development Group to consider the thorough evaluation of GALFAN. This will result in a 100-day Arizona proving ground test being undertaken. However, this work is contingent upon successful completion of spotwelding tests. Mr. Roberts had found very recently that material sent to Ford for evaluation had failed the spotwelding tests but not by a large degree. He anticipated that the characterization of GALFAN at Ford would probably continue.

The Sheller-Globe Truck & Body Division is also evaluating the use of GALFAN for truck cabs and for this purpose, is evaluating the paintability of GALFAN with automotive paints. The cathodic electrocoating system used by Ford will be used during their tests. At Butler Manufacturing, both prepainted and unpainted GALFAN material has been received for evaluation. The unpainted material will be painted by Butler suppliers. Materials will then be put out on long-term exposure testing and compared to other substrates for use in metal building applications. At Stelco and Dofasco, metal buildings have been constructed with coil coated material and will be evaluated in future years.

Mr. Roberts noted that the coil coating of GALFAN is very similar to the coating of galvanized steel. There are minor adjustments which need to be made to the normal coil coating process. No chromate passivation should be used with GALFAN, a stronger alkaline clean is needed, and a phosphate not a chromate pretreatment is used. If zinc phosphatizing is used, the surface should be activated previously.

Mr. Celestin noted that some people need to do post painting instead of coil coating. He asked if anybody else had used an iron phosphate pretreatment. Mr. Matthews replied that British Steel had probably used it in their early work on Ziegler material and that it was generally successful. Mr. Celestin asked if a chromated GALFAN material could be used to build a metal building and then painted successfully in later years. As the answer to this question was not known, Mr. Matthews asked if a hot-dip galvanized building could be painted after two years of exposure if it was initially chromated. Mr. Skenazi noted that the rate of chromate weathering on GALFAN was being examined under work in progress. Thus, a satisfactory answer to this question was not obtainable at this time. Mr. Hirose asked if the Ford tests were being carried out on exposed or unexposed panels. Mr. Roberts replied that they were being done on unexposed panels.

Mr. Buscarlet noted that regarding Mr. Roberts' suggestion that a stronger alkaline clean be used, this problem was also being studied at Ziegler. They think the alkaline cleaner must be weaker rather than stronger to prevent edge corrosion. They have seen a better edge performance with weaker alkaline cleaners than strong alkaline cleaners. Mr. Roberts replied that according to the coil coaters which are cooperating on this investigation, oil and the thin aluminum film have to be removed from the surface of the GALFAN coating. Mr. Buscarlet asked if any lab had confirmed. Mr. Roberts replied that Parker and Heatbath had carried out this work. Mr. Buscarlet indicated his interest in confirming this result.

Pretreatments From Procoat

Mr. Brugarolas noted that his company was looking at new inorganic coatings which would produce the gray patina produced on GALFAN. Photographs were shown of the effectiveness of this pretreatment on GALFAN in various atmospheres. He noted that chromates are not good components to prevent gray patina on GALFAN. He desired to produce a produce without chromate and a treatment using only organics was now available and had been used to produce the results shown. He had worked with CRM to produce the samples and found that good results were obtainable. Using a humidity cabinet at 50 degrees C and 90% humidity, it was found that no gray patina was found after 150 hours. He volunteered to work with any company interested in trying this new product.

Undervehicle Testing In Canada

Dr. Goodwin noted that a recent paper had been published as a result of a presentation by Dofasco at an American Society for Metals Conference. This reviewed their extended exposure of GALFAN, galvanized, galvalume and electrogalvanized coatings on vehicles which ran along the highway in Canada. A copy of this paper is attached to these minutes. He also noted that Baycoat had installed a new roof on their building in Hamilton, Ontario, Canada. This building featured six (6) different coatings on its roof. It had painted and unpainted GALFAN, galvalume, galvanized steels on its roof. This produced a "zebra" roof, which will be subject to exposure for many years in this industrial atmosphere. This should yield good corrosion performance data on all these coatings. The GALFAN used during this testing was bought from Nisshin Steel and coil coated at Bycoat.

Mr. Roberts asked further about the painting tests which had been done at Ziegler. Mr. Buscarlet replied that the test used was a salt spray test on the painted panels of GALFAN. Edge creep after salt spray was measured and used as an indicator of quality.

SPOTWELDING RESEARCH

Mr. Roberts reviewed various effort on spotwelding of GALFAN which were going on around the world.

ILZRO's project, ZM-324, will be concluded during 1986. It has been going on for several years and has been examining the effect of materials variations, process variations and dynamic inspection monitoring on the spotwelding process. Variations in materials is examined during this research are roughness, coating thickness, coating structure, and coating chemistry. Process variations examinedwere current sloping, electrode geometry, and the use of preheating and potheating. Both truncated cone and domed electrodes were used in the tests. The welding lobes for GALFAN-coated sheet were shown. These are attached to these minutes. It was found that the use of upsloping and downsloping of the current improved the range of weld currents which could be used to give good welds. Mr. Roberts noted sloping of the current did not give any benefits on galvannealed materials using the truncated cone electrode. Dynamic inspection monitoring was found to be of benefit in understanding the spotwelding process. Graphs of the displacement and current versus cycles, which is equivalent to time, were shown. These are also attached to these minutes. Work during 1985 and 1986 in this project will characterize electrogalvanized, hot-dip galvanized products using some of the above process variations and examining the effect of materials variations. Electrogalvanized steel has been obtained from Armco, Bethlehem Steel, National Steel and Nippon Kokan.

Mr. Roberts then showed a video cassette of highspeed filming of welds using various types of process variable which had been made at MIT. Using a 24-cycle weld time, cycles of upslope, downslope and preheat were added to the basic weld cycle. The effect of these modifications on zinc expulsion and weld quality could be seen.

Mr. Roberts also noted that different electrode shapes give different heat patterns in the spotwelding process. The investigators at MIT have found that heating tends to concentrate along the outer circumference of the electrode in the truncated geometry. This results in the highest temperatures at these points and results in the electrode wear being the worst at these points. It also results in the outer part of the nugget being formed first which can inhibit zinc expulsion.

Mr. Roberts also briefly reviewed work previously carried out or going on currently at other laboratories. At CRM, he noted that the effect of electrode shape and cooling of the electrode had been correlated with electrode life. At Thyssen, this had been carried further in examining the spotweldability of GALFAN with a harder electrode using the same electrode geometry in use at CRM. National Steel in the USA has examined the tip-life of a normal automotive called electrode with GALFAN and has had poorer results. He noted that General Motors has incorporated upsloping as developed during the MIT project into their welding practice. As reported in a past licensees meeting, Hoesch has done some work on spotwelding of GALFAN and has other work going on at the present time. Ford's work was also reviewed previously during this meeting and is not terribly encouraging, however, new material may solve this problem. In related work, a cooperative project between ILZRO, Nippert and Sheller-Globe is examining the use of a titanium diboride dispersion strength electrode which had been developed during an ILZRO-sponsored project at Amax. This has been extruded into shape by Outokumpu in Finland and machined into electrodes by Nippert in the USA. The characterization of this electrode will be done by Sheller-Globe very soon.

Mr. Celestin asked if anyone had studied the adhesive bonding characteristics with GALFAN. Mr. Skenazi noted that nothing had been done for ILZRO but other studies were going on. Mr. Matthews noted that British Steel is looking at adhesive bonding of coated steel under pressure from the British automotive companies. Adhesive bonding will not be used alone, but rather it will used in conjunction with welding to assemble automobiles five years from now, they believe. Mr. Toomer asked about the details of the Ford spotwelding tests and Mr. Roberts replied that it involved 2,000 consecutive spotwelds on a single electrode tip. It is required to obtain a specified weld diameter without regressing the tip or changing the settings on the weld machine to pass this test. Mr. Toomer asked if other types of welding were being examined by anyone on GALFAN. Mr. Roberts replied that Ford will do seam welding and compare it with terne coating to see if GALFAN can be substituted for a gasoline tank fillerneck. Mr. Coutsouradis added that there were several places in France and Belgium where adhesive bonding was being examined. A variety of results have already been seen.

## PATENTS AND TRADEMARK STATUS

Dr. Goodwin reviewed the status of patents and trademarks on GALFAN. A summary on this, prepared by Dr. Carr of ILZRO, is attached to these minutes.

## MEETING ADJOURNED

There being no further business, this meeting was adjourned by Dr. Goodwin at 5:30 p.m.

ILZRO PROJECT ZM285

# GALFAN - CORROSION REPORT.

by A. SKENAZI, B. RENAUX, A. DAVIN - C.R.M.

## Objective.

Corrosion of Galfan in an industrial atmosphere.

## Experimental procedure.

Exposure of Galfan coated samples (150x200mm) on the roof of the CRM-building in Liège during the period of October 31, 1984 to October 21, 1985.

The thicknessloss was determined by the Anderson-Reinhard method (pickling for 3 minutes in a 80 g/l $CrO_3$ solution at 80°C and dividing the weightloss by the density of Galfan (6.6)).

The experimental results allow to determine the effect of chromating (Cr), temperrolling (SKP) and eutectic coating structure (ph). The detrimental effect of a heavy gage steel was set on 0.65 µm.

Each value corresponds to two experiments.

## Experimental results (Anderson - Reinhard Method).

| N° | Coating | Cr | SKP | ph | E (µm) |
|---|---|---|---|---|---|
| 1 | Galfan | - | * | - | 1.35 |
| 2 | Galfan | - | * | - | 1.20 |
| 3 | Galfan | - | - | - | 1.34 |
| 4 | Galfan | * | * | - | 0.98 |
| 5 | Galfan | * | * | - | 1.17 |
| 6 | Galfan | * | * | * | 1.36[@] |
| 7 | Galfan | * | - | - | 1.18 |
| 8 | Galfan | * | - | * | 0.79 |
| 9 | Galvanized | * | - | | 1.65 |
| 10 | Galvanized | * | - | | 2.35 |
| 11 | Galvalume | - | * | | 0.63 |

@ heavy gage : 2.35mm (impact on corrosion rate 0.65 µm)
* : yes - : no

## Conclusion :

| | |
|---|---|
| Effect of SKP | 0.08 µm |
| Effect of Cr | 0.18 µm |
| Effect of ph | 0.39 µm |
| Effect of edge | 0.65 µm |

| | |
|---|---|
| Minimum annual corrosion for Galfan | 0.70 ± 0.07 µm |

# 7TH GALFAN MEETING

## BRUSSELS, DECEMBER 1985

## C.R.M.

## RESEARCH REPORT

1. CORROSION
2. SINGLE DIP PROCESS
3. REVIEW 1985 ACTIVITIES

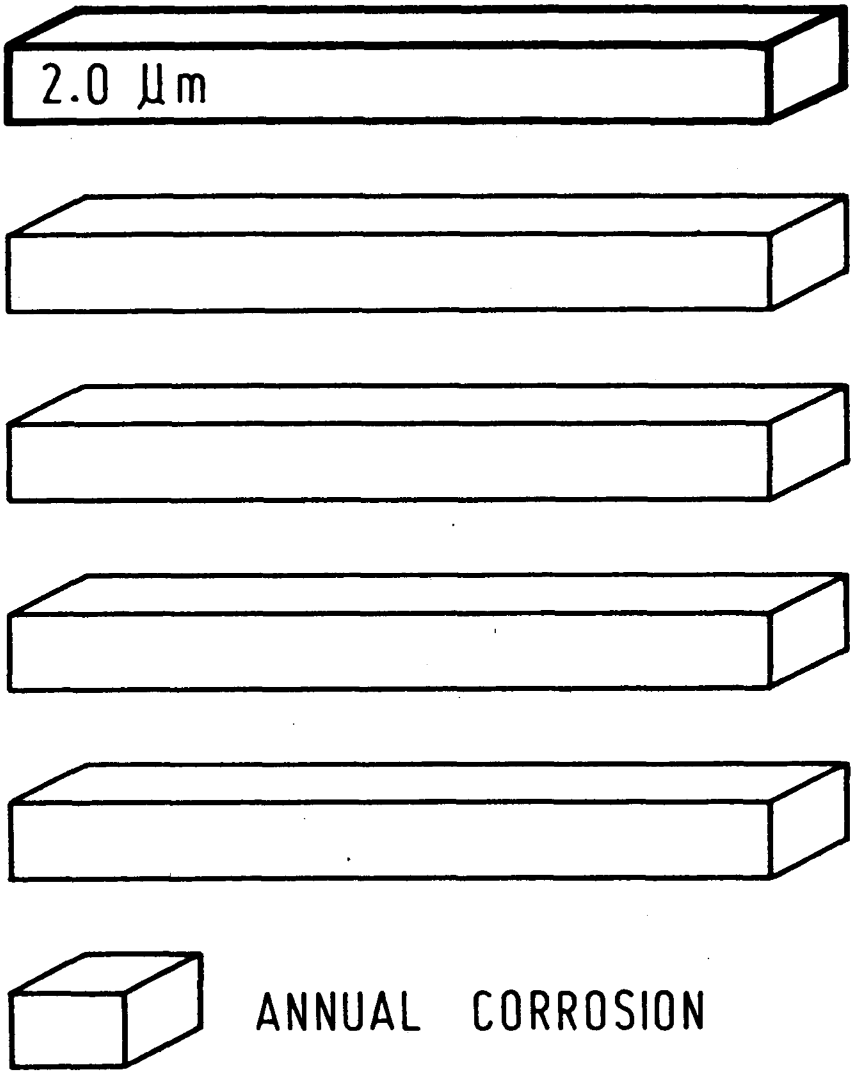
# 7TH GALFAN MEETING
## C.R.M.

## CORROSION REPORT

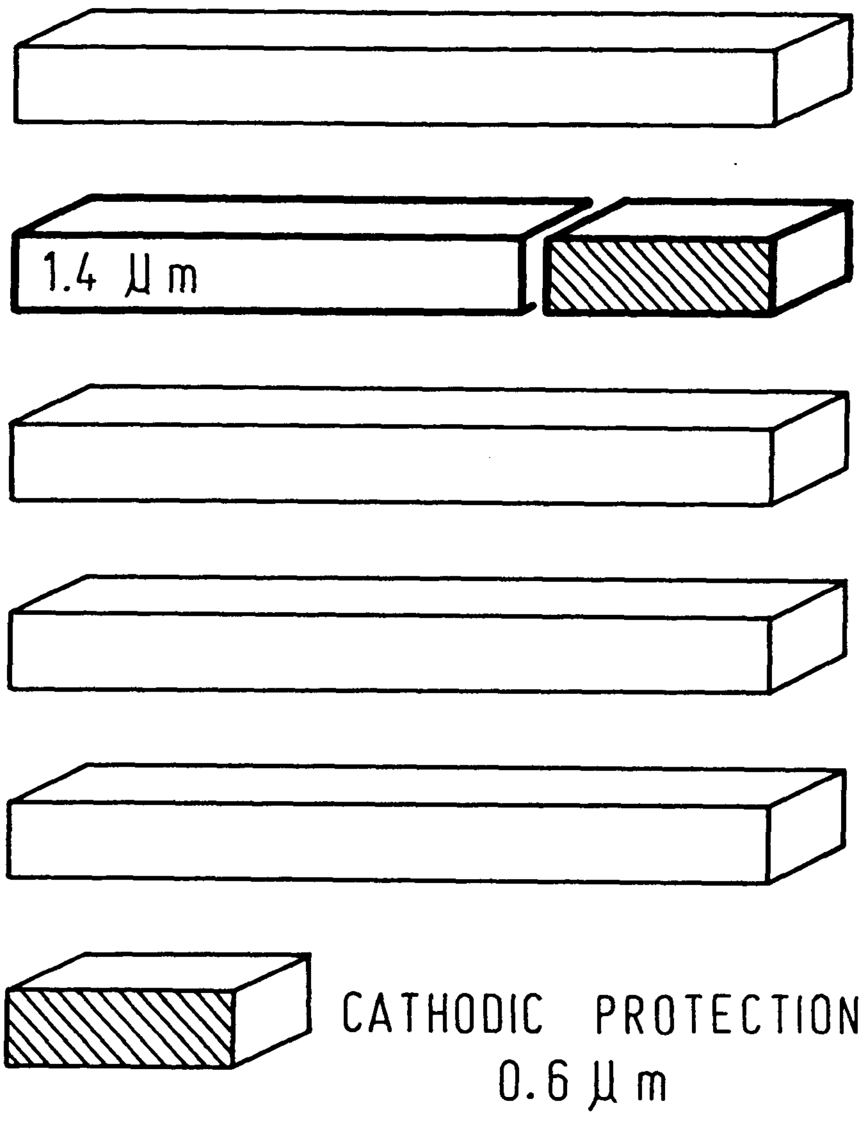
PREVIOUSLY REPORTED CORROSION DATA (INDUSTRIAL ATMOSPHERE).

| ZINC | ZN-5% AL | ZN/ZNAL | SOURCE |
|---|---|---|---|
| 1.8 μM | 1.6 μM | 1.12 | CRM (1 YEAR) |
| 3.8 μM | 3.5 μM | 1.08 | V.M. (3 YEARS) |
| 3.6 μM | 3.5 μM | 1.03 | CRM (2 YEARS) |
| 8.0 μM | 6.0 μM | 1.33 | BETHLEHEM STEEL (5 YEARS) |
| 3.4 μM | 2.2 μM | 1.55 | NIPPON STEEL (3 YEARS) |

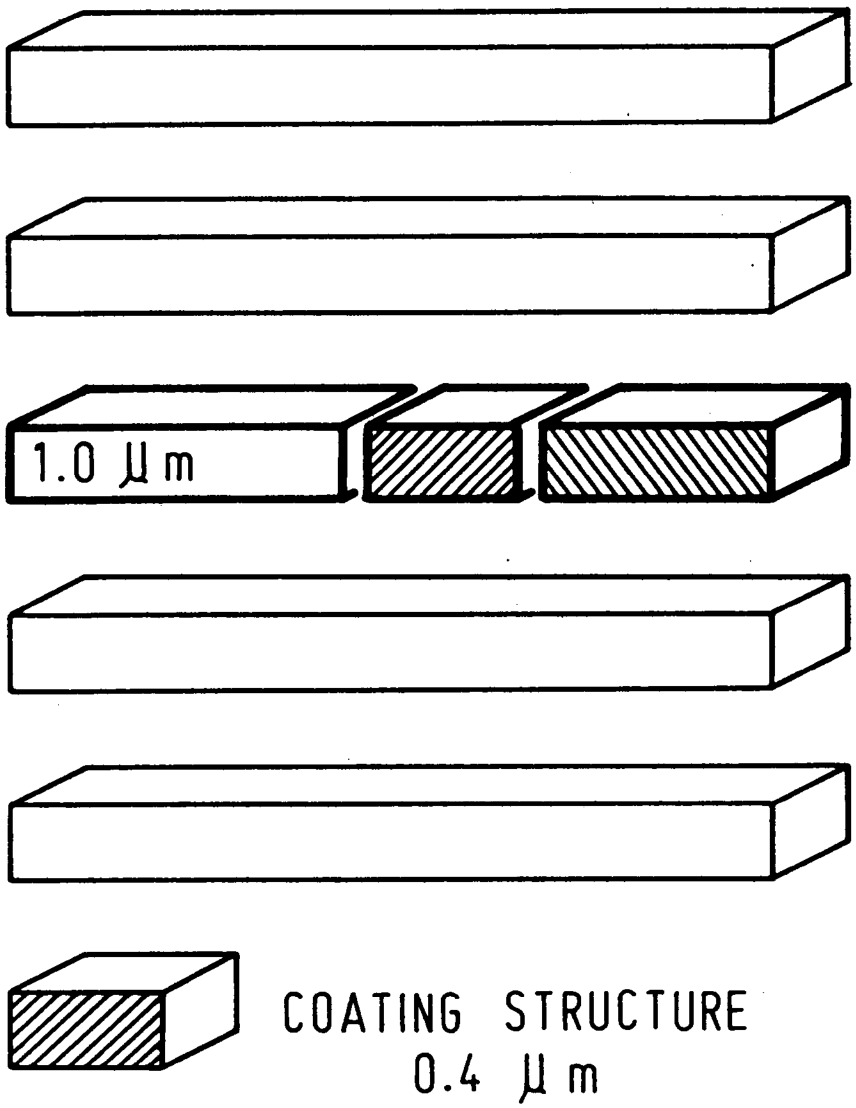
EXPOSURE IN INDUSTRIAL ATMOSPHERE GALFAN



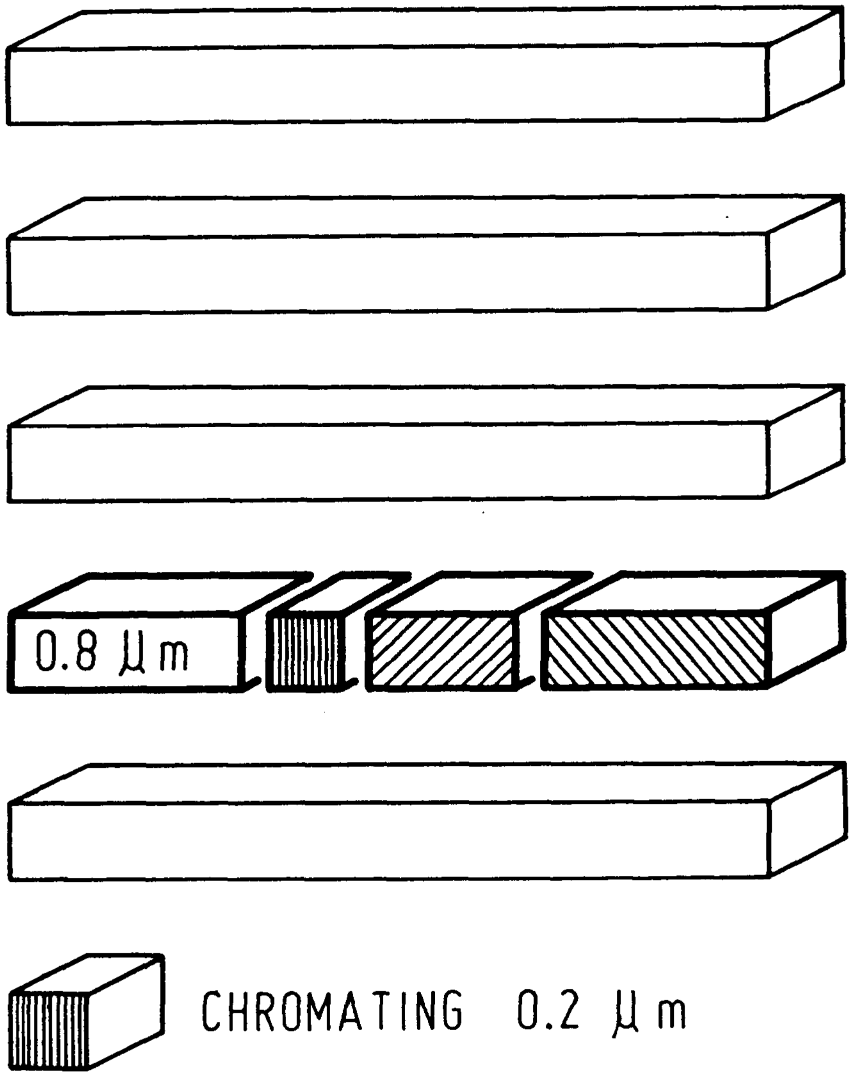
EXPOSURE IN INDUSTRIAL ATMOSPHERE GALFAN



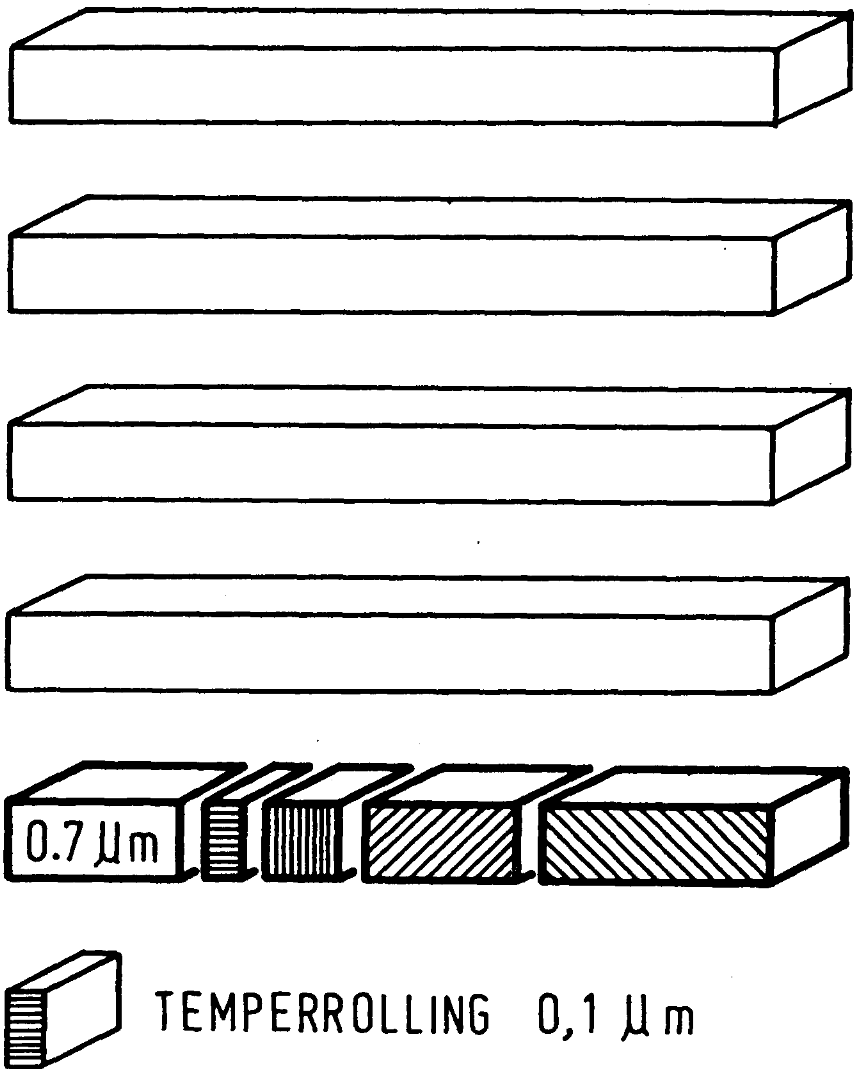
EXPOSURE IN INDUSTRIAL ATMOSPHERE GALFAN



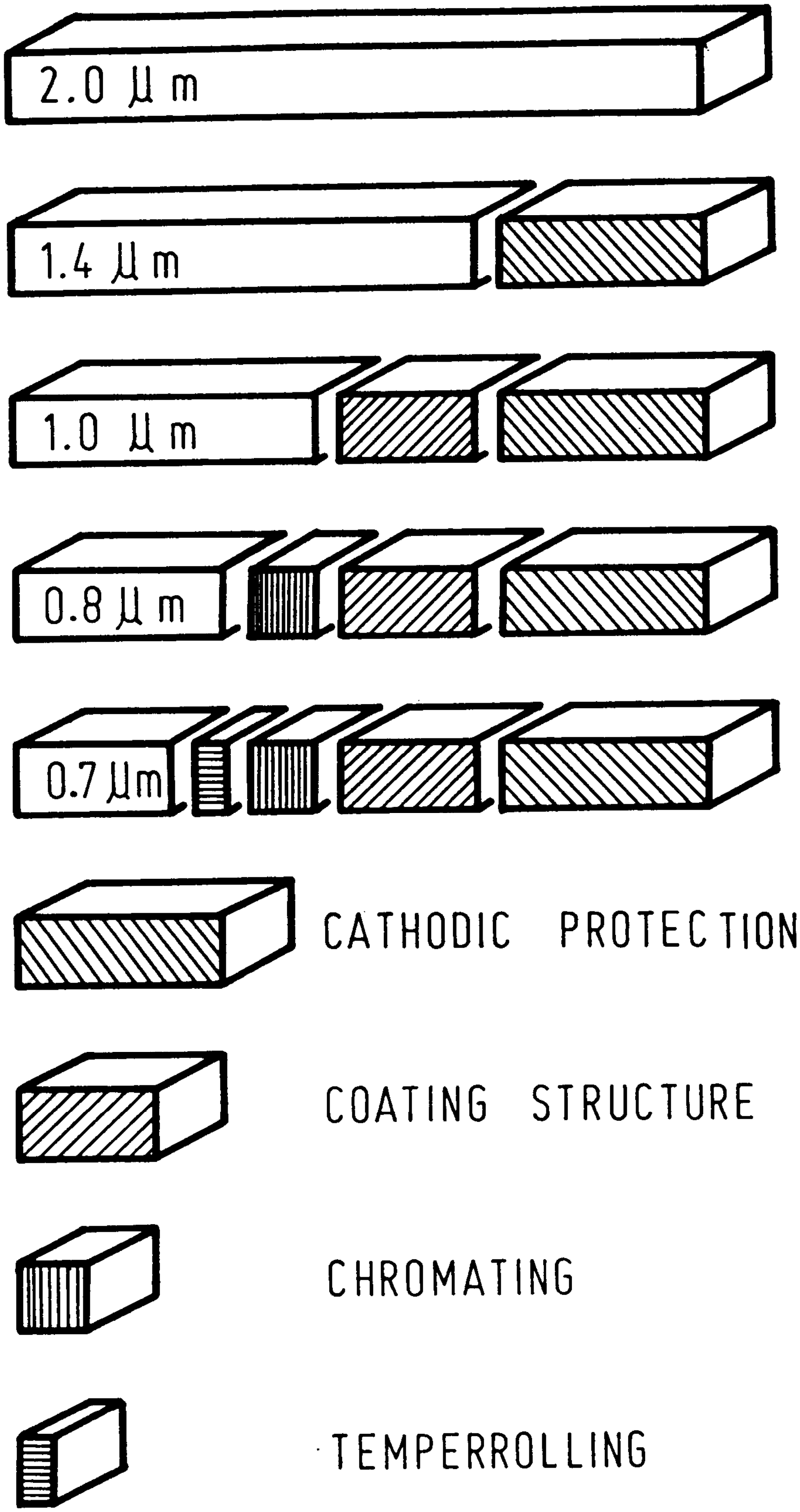
EXPOSURE IN INDUSTRIAL ATMOSPHERE GALFAN



# EXPOSURE IN INDUSTRIAL ATMOSPHERE GALFAN



EXPOSURE IN INDUSTRIAL ATMOSPHERE GALFAN



# 7TH GALFAN MEETING
# C.R.M.

## CORROSION REPORT

## FACTOR ANALYSIS

$X = F\ (A, B)$

$A = A\ (+, -)$

$B = B\ (+, -)$

| TEST | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| A | + | + | - | - |
| B | + | - | + | - |
| X | $X_1$ | $X_2$ | $X_3$ | $X_4$ |

7TH GALFAN MEETING
C.R.M.

CORROSION REPORT

EXAMPLE.

X : CORROSION RESISTANCE

A : COATING STRUCTURE
+ EUTECTIC
- NON EUTECTIC

B : SURFACE FINISH
+ TEMPER ROLLED
- REGULAR SPANGLE.

7TH GALFAN MEETING
C.R.M.

CORROSION REPORT

| TEST | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| A (PH) | + | + | - | - |
| B (SKP) | + | - | + | - |
| X (μM) | 0.7 | 0.8 | 1.1 | 1.2 |

CONCLUSION

A(PH) 0.4 μM

B(SKP) 0.1 μM

## 7th GALFAN MEETING
## C.R.M.

### CORROSION REPORT

| | Annual corrosion (Liège) | |
|---|---|---|
| | Unchromated | Chromated |
| Galvanized | - | 2.0 µm |
| Galfan | 1.2 µm | 1.0 µm |
| Galvalume | 0.6 µm | - |

## 7th GALFAN MEETING
## C.R.M.

### CORROSION REPORT

| Coating | Corrosion resistance | Cathodic protection | Ductility |
|---|---|---|---|
| Galvanized | 100 | Good | Good |
| Galfan | 200 | Good | Excellent |
| Galvalume | 400 | Fair | Good |

# 7TH GALFAN MEETING
# C.R.M.

## DARKENING OF GALFAN

| REFLECTANCE OF | BEFORE<br>ONE YEAR EXPOSURE | AFTER<br>ONE YEAR EXPOSURE |
|---|---|---|
| UNCHROMATED GALFAN | 40% | 25% |
| CHROMATED GALFAN | 50% | 35% |
| CHROMATED GALVANIZED | 50% | 35% |
| UNCHROMATED GALVALUME | 90% | 60% |

* REMARK : REMAINING REFLECTANCE OF UNCHROMATED GALFAN AFTER 10 DAYS EXPOSURE IN HUMIDITY CABINET (95°C - 95% RH) IS 15%.

7TH GALFAN MEETING

C.R.M.

# METALLOGRAPHIC STUDY OF GALFAN

## INITIAL COATING STRUCTURE.

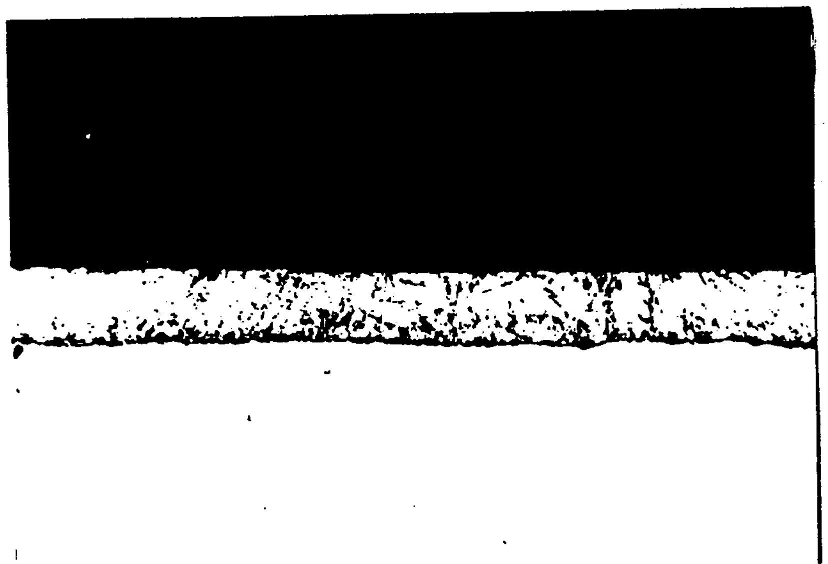
## COATING STRUCTURE AFTER ONE YEAR EXPOSURE.

7TH GALFAN MEETING

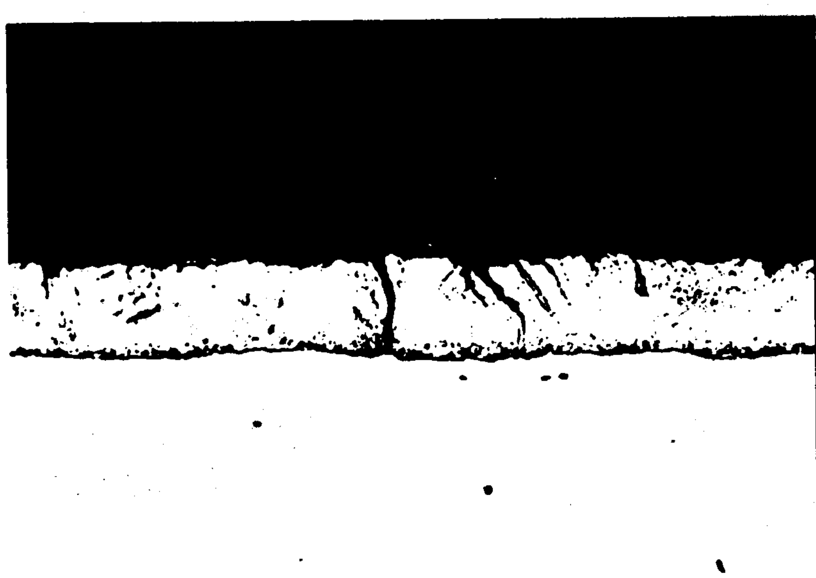
C.R.M.

## METALLOGRAPHIC STUDY OF GALVANIZED.

INITIAL COATING STRUCTURE.



COATING STRUCTURE AFTER ONE YEAR EXPOSURE.

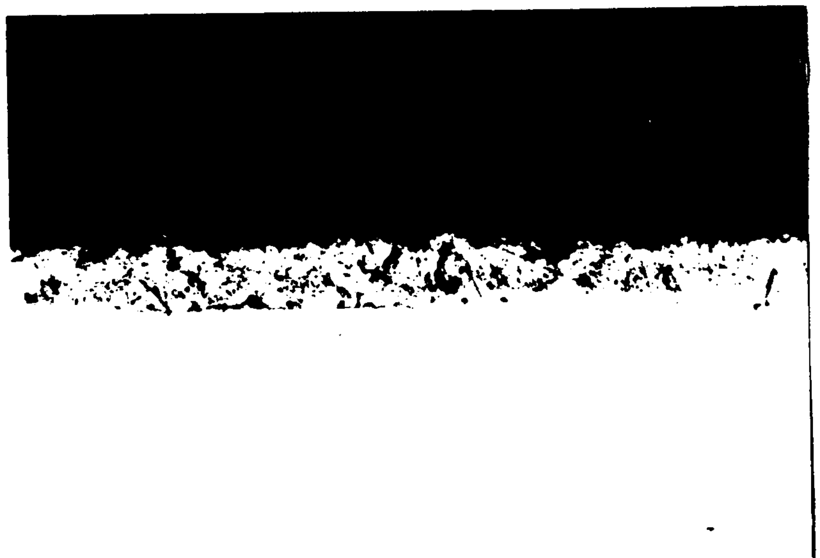


# 7TH GALFAN MEETING

## C.R.M.

## METALLOGRAPHIC STUDY OF GALVALUME

INITIAL COATING STRUCTURE.



COATING STRUCTURE AFTER ONE YEAR EXPOSURE.

7TH GALFAN MEETING
C.R.M.

# LIMITING DOME HEIGHT.

## TEST CONDITIONS

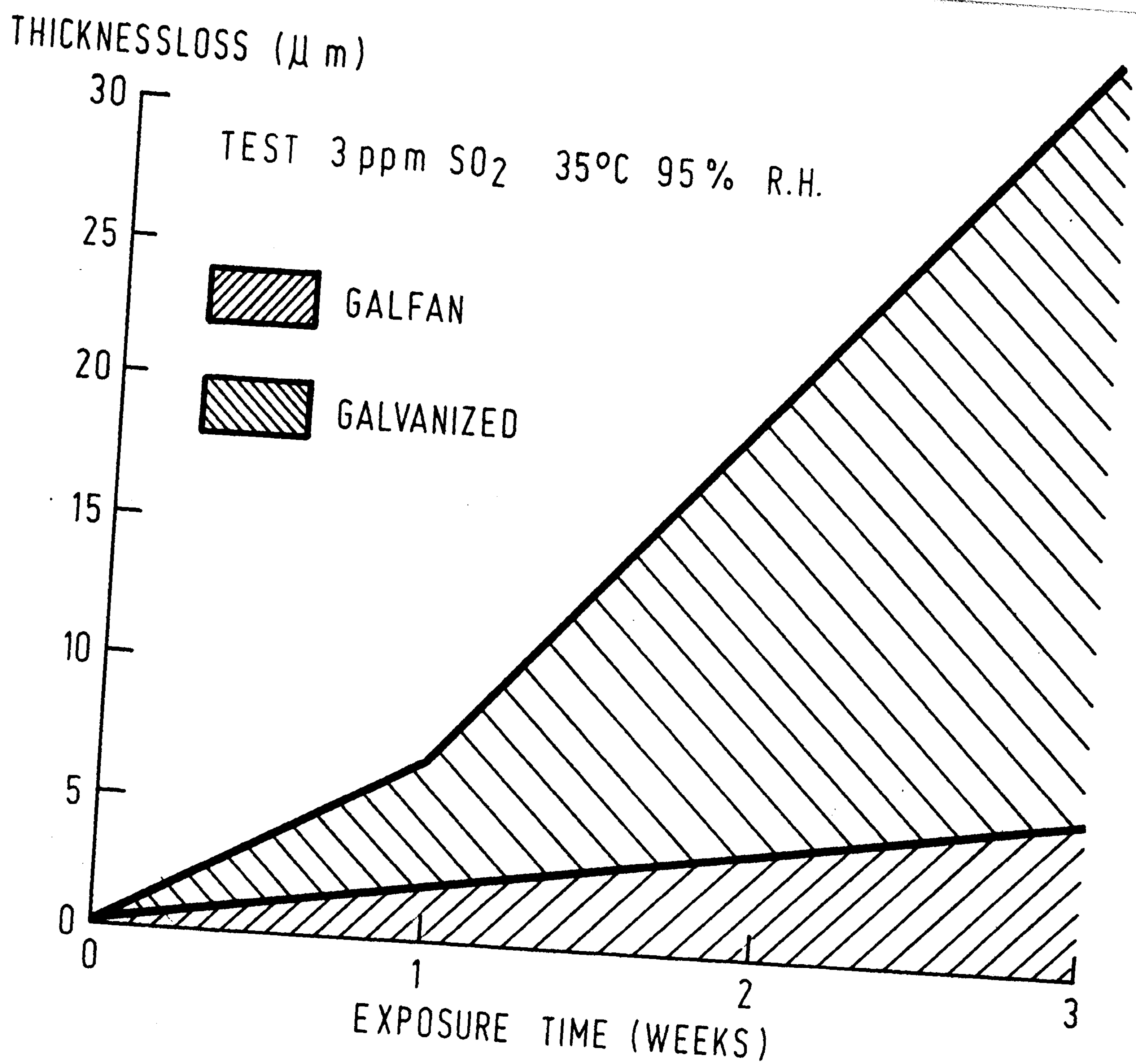
* NUMBER OF TESTS :7
* WITHOUT LUBRIFICATION
* DIE DIAMETER : 110MM
* WIDTH OF PANEL : 130MM

## TEST MATERIAL

* STEEL ST 05 Z
* CAOTINGS : 1) GALFAN 275 $G/M^2$
  2) GALVANIZED 275 $G/M^2$

## TEST RESULTS.

| COATING | $(LDH)_0$ MM |
|---|---|
| GALFAN | 48.1 ± 0.8 |
| GALVANIZED | 46.7 ± 0.7 |



THICKNESSLOSS (μm)
30
25
20
15
10
5
0
TEST 3 ppm $SO_2$ 35°C 95% R.H.
GALFAN
GALVANIZED
0
1
2
3
EXPOSURE TIME (WEEKS)

*7th GALFAN MEETING*

*BRUSSELS, December 5-6, 1985*

*CRM Report on*

# *EVALUATION OF GALFAN COATED WIRE BY A SINGLE DIP PROCESS.*

*by A. SKENAZI, B. RENAUX, A. DAVIN (C.R.M.)*

## *INTRODUCTION.*

*Improved corrosion resistance and superior formability provide the two major incentives for the development of Galfan. The implementation of the eutectic zinc-aluminium bath in continuous sheet galvanizing proved to be successful with several commercial producers in Japan, France and Germany.*

*In wire galvanizing a quite different way of processing is used i.e. a chemical surface preparation by fluxing. The incompatibility of the conventional $ZnCl_2$-$NH_4Cl$ fluxes with zinc-aluminium baths gave rise to the development by CRM of the so-called double dip process . The first Galfan licensee to apply this process was the French compagny FICAL.*

*From a technical and an economical point of view a strong need remained for the development of a single dip process with Galfan. The most straightforward approach consisted in requesting the collaboration of flux manufacturers for the development of fluxes compatible with the Galfan bath. In spite of the large variety of fluxes evaluated at CRM or with the cooperation of TECHNOARBED, Luxembourg, it was not possible to achieve a coating soundness equivalent to that of the double dip processed Galfan coating. A combination of the double and the single dip has also been evaluated. This combination consisted of the electrodeposition of a zinc layer prior to the immersion of the wire in the Galfan bath. Technical and economical drawbacks proved to be too important, so only laboratory trials were performed.*

*It was observed that, with various plating baths based on $ZnSO_4$ or $ZnCl_2$, a thickness of 10µ for the zinc electrodeposited layer was necessary to obtain a good coating.*

*The low reactivity of the Galfan alloy towards steel and the unsufficient wetting even for some special fluxes should be counteracted. The development of a continuous process is of course limited in the possibilities. In fact there are no means to change drastically the surface preparation of the wire except for the cleaning of the steel wires before fluxing (for instance longer pickling times and higher HCl acid concentrations). The first trials showed that no substantial increase in the wetting of the steel wire or in the surface quality were observed.*

*A single dip process was therefore developed aiming at overcoming the shortcomings of the approaches mentionned above.*

*In this presentation we shall describe the characteristics of the single dip coating and the properties of the single dip processed wires in comparison with the double dip wires.*

## *THE SINGLE DIP PROCESS.*

*The processing sequence for the single dip process is quite similar to that in current lines. This results in an easy implantation of the process on existing lines.*

*The process was investigated in the laboratory and recently its feasibility under industrial conditions was confirmed in cooperation with TechnoArbed, Luxemburg.*

*The steps of the process are the following :*

1) *pickling in hydrochloric acid (at least 15%)*
2) *special fluxing*
3) *drying*
4) *immersion in Galfan bath.*

*Under industrial conditions a lead patenting operation is required to obtain certain mechanical properties. This nevertheless constitutes a real danger of lead contamination of the Galfan bath via transport by the wire.*

*Pickling in hydrochloric acid is mandatory to clean the steel wire efficiently. It is recommended that the concentration of the acid is at least 15% and preferably higher. Although not investigated, electrolytic pickling should also be a valid solution.*

*A study of different fluxes was undertaken in the laboratory especially with the meniscograph technique in order to determine the optimum conditions for applying the single dip process.*

*The compositions of the investigated commercial fluxes were all proprietary. Some of the fluxes used were reported to contain fluorides and/or wetting agents whereas others were reported to be free from either or both of these additions. The results of the meniscograph studies showed that for normal fluxing conditions a wetting force of the order of -300 dynes is observed. The addition of wetting agents made it possible - under the same conditions - to increase the wetting force to +300 dynes. With the single dip process developed the wetting force increased to values between 700 and 1000 dynes. It is also important to note that the single dip process developed allows to use fluxes which were shown to be completely unappropriate in normal conditions.*

## *ENVIRONMENTAL CONSIDERATIONS.*

*The use of certain fluoride-containing fluxes might cause environmental concern.*

*The existing legislation for instance in Belgium and in the USA limit the fluoride level in waste water to 40 mg/l, which is most certainly exceeded for most fluxes intended for Galfan.*

*Concerning the emission of fluorides in the ambiant air the following maximum values are given : for Belgium 2.5 mg/m$^3$, for USA 2.0 mg/m$^3$ and for Western Germany 5 mg/m$^3$.*

*To meet such concern from galvanizers it appeared warranted to evaluate the performance of some fluxes reported to contain no fluorides.*

## *INDUSTRIAL TRIALS.*

*Industrial trials were performed in cooperation with TechnoArbed, Luxembourg having in mind the results observed during the laboratory trials at CRM. In a first stage, single dip trials were performed using different fluxes as earlier reported. In general the Galfan coated wire obtained presented a lot of defects. The principal coating defects observed thus far were related to unsufficient pickling (bare spots - uncoated areas), formation of flux residues on the bath (black embedded flux residues - increased roughness) and too important reactivity (holes in the coating).*

*A classification of different fluxes was made previously based on the final coating quality obtained by the normal fluxing process. The ratings given to the different samples ranged from 1 to 6. The value of 9-10 was given to the double dip sample. Industrial trials performed with the single dip process developed, showed a better quality of the Galfan coated wire and ratings from 8 to 10 for fluoride containing fluxes and from 5 to 7 for fluoride-free fluxes were obtained.*

## *COATING CHARACTERIZATION.*

*The different coatings were characterized as follows :*

1) *metallographic study of the coating structure*
2) *coating weight*
3) *the coating uniformity (immersion in $CuSO_4$ solution)*
4) *the formability (ductility testing)*
5) *intergranular corrosion resistance*
6) *salt spray testing*
7) *Kesternich testing*
8) *3ppm $SO_2$ testing*
9) *atmospheric exposure.*

*The metallographic study revealed the typical coating structure of Galfan with the eutectic matrix in which zinc primary crystals could be found.*

The coating weight was 260 $g/m^2$, corresponding to 40 μm thickness. This coating weight was obtained with a line speed of 24 m/min.

The coating uniformity test by an immersion in a $CuSO_4$ solution showed a behaviour similar to the Galfan coating obtained by the double dip process except in some instances for which non uniformity could be ascribed to particular experimental conditions.

The excellent formability of Galfan coating was demonstrated by the wrap up test around one time the diameter, without any cracking.

The intergranular corrosion, which is induced by an excessive lead contamination of the Galfan bath, can be demonstrated by a hot humidity test, followed by a wrap up test. A significant decrease in the intergranular corrosion was observed with the single dip Galfan coated wires, compared to the double dip Galfan. Macrographs of the deformed Galfan coated wires show that no cracking occurs in the as coated condition or after the humidity testing.

The corrosion resistance of the Galfan coated wires was determined by accelerated tests.

The neutral salt spray test confirmed the superior corrosion resistance of Galfan over galvanized. The differences observed between the single dip and the double dip are not sufficiently important to conclude that the intermetallic layer at the interface for the double dip coated wires increases to any extent the corrosion resistance.

The Kesternich test did reveal a higher corrosion resistance for double dip material (more than 25 cycles before 100% red rust) compared to the single dip one (with 22 cycles to 100% red rust). Further tests are being performed in order to confirm this behaviour.

The 3 ppm $SO_2$ test revealed that the corrosion rate of Galfan (independently from the way of processing) is inferior to 2 μm/week. For galvanized the corrosion rate is more than 6 μm/week. These data were *recorded for a test period of three weeks. It should be kept in mind that the initial coating thickness was 40µm. In this way it was not possible to take into account the effect of the intermetallic layer formed during the double dip process.*

*The atmospheric exposure of Galfan coated and galvanized wires are underway. The major differences observed during the first months of exposure are the formation of white rust on galvanized wires and the darkening of Galfan.*

## CONCLUSIONS.

*The development of a single dip process for Galfan coated wires is based on the experience gained by CRM with the evaluation of different fluxes and other processes studied as an alternative to the double dip process.*

*The application of this single dip process makes it possible to produce a Galfan coating of at least the same quality as the double dip one and to widen the operation margins for flux density, fluxing temperature, iron contamination, pickling conditions, etc.*

*The process can be adapted to existing lines, although it should be kept in mind that the processing parameters have to be adjusted depending on the fluxes used and on the line characteristics.*

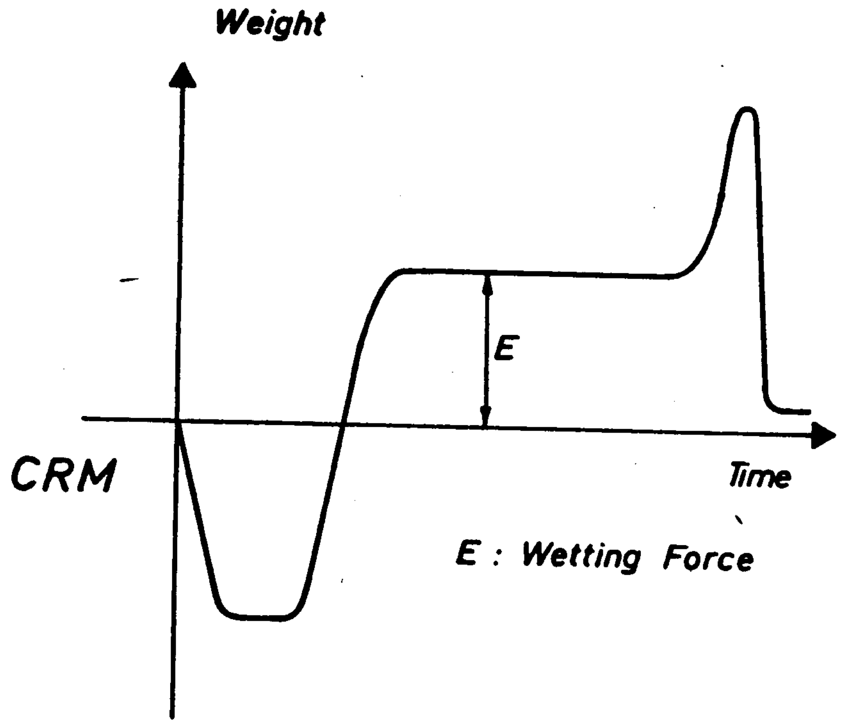
*The coating structure corresponds to the typical hypoeutectic Galfan structure with zinc rich globules in a eutectic matrix.*

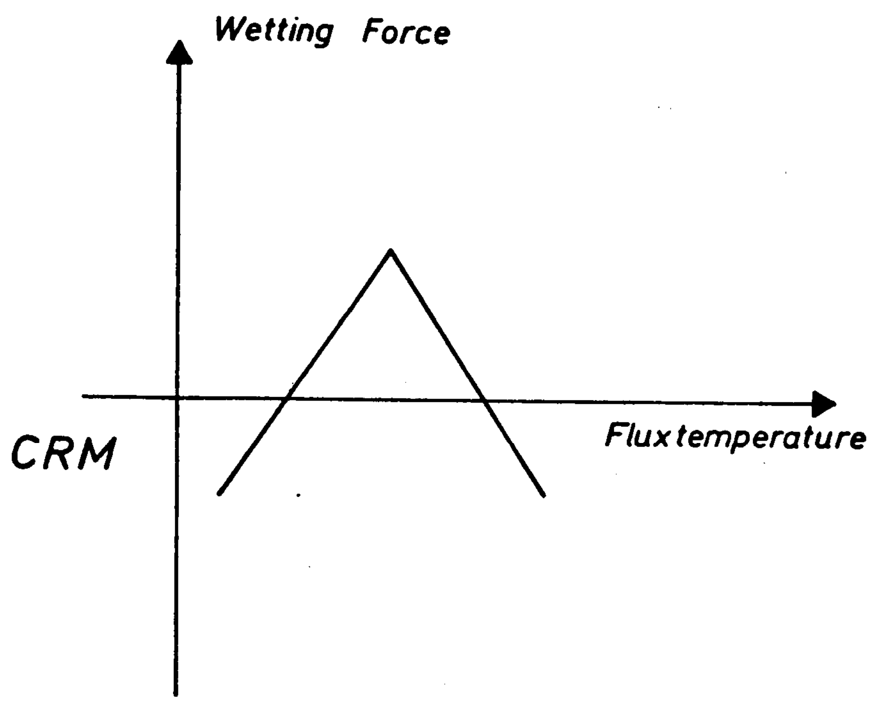
*The performance of the single dip Galfan proved to be better as far as ductility is concerned especially after humidity testing compared to the double dip coating (no intergranular corrosion is observed). The corrosion rate of this product is equivalent to that of the double dip product.*

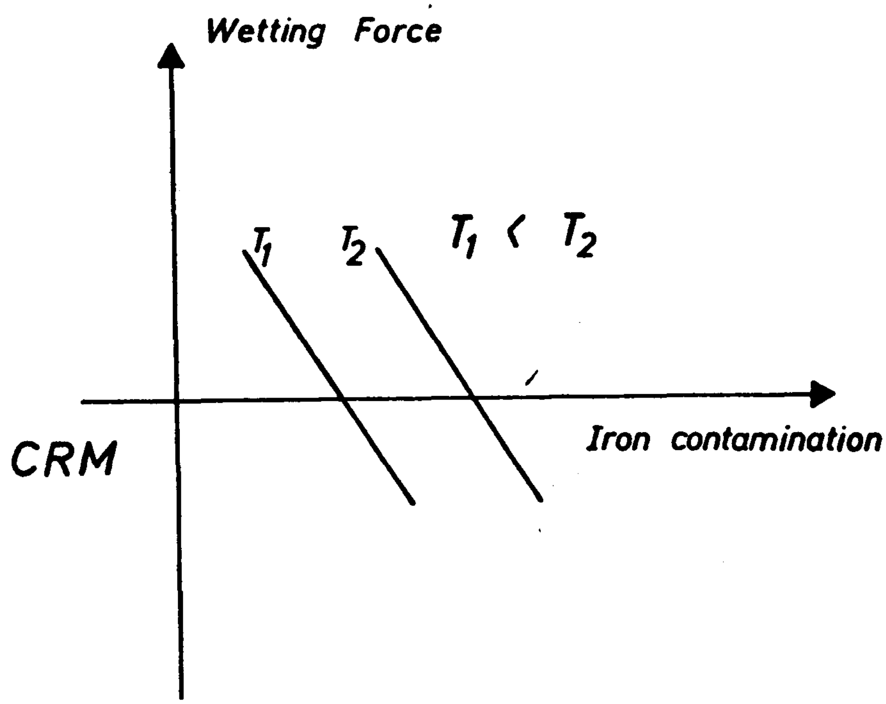
*The corrosion testing confirmed previous results as far as the comparison to galvanized with a corrosion resistance which is 2 to 3 times higher for Galfan.*

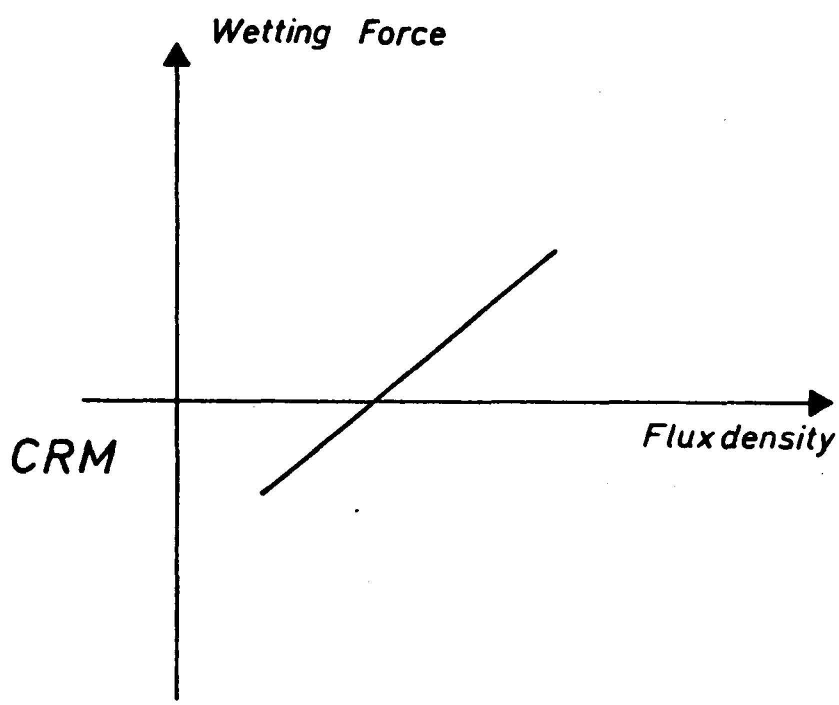
*With the actual status in the development of a single dip process it is possible to produce industrially Galfan coated wires with characteristics which are superior to galvanized.*

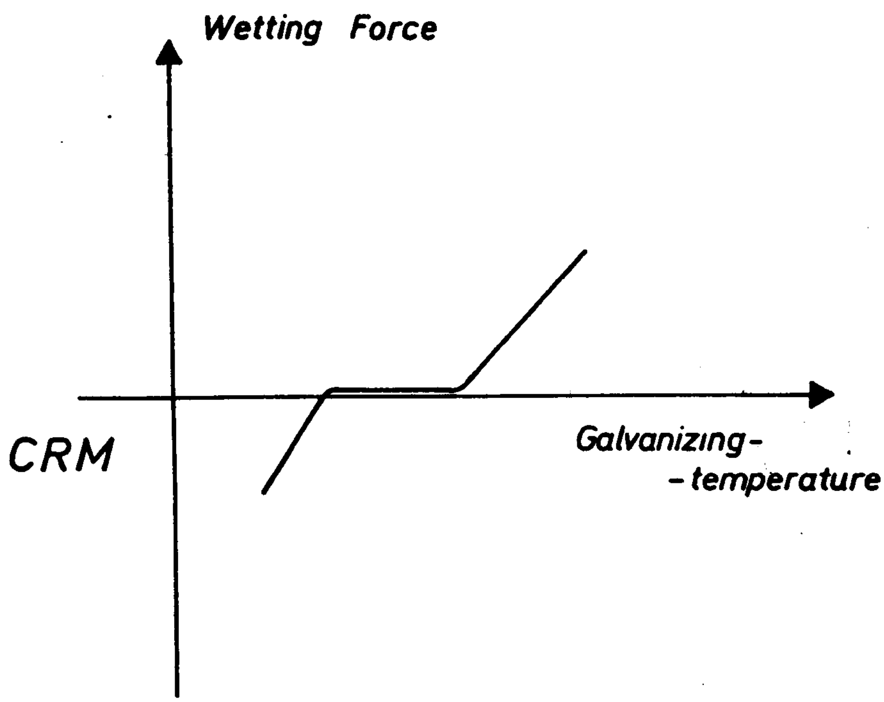
*C.R.M.*
*December 1985.*

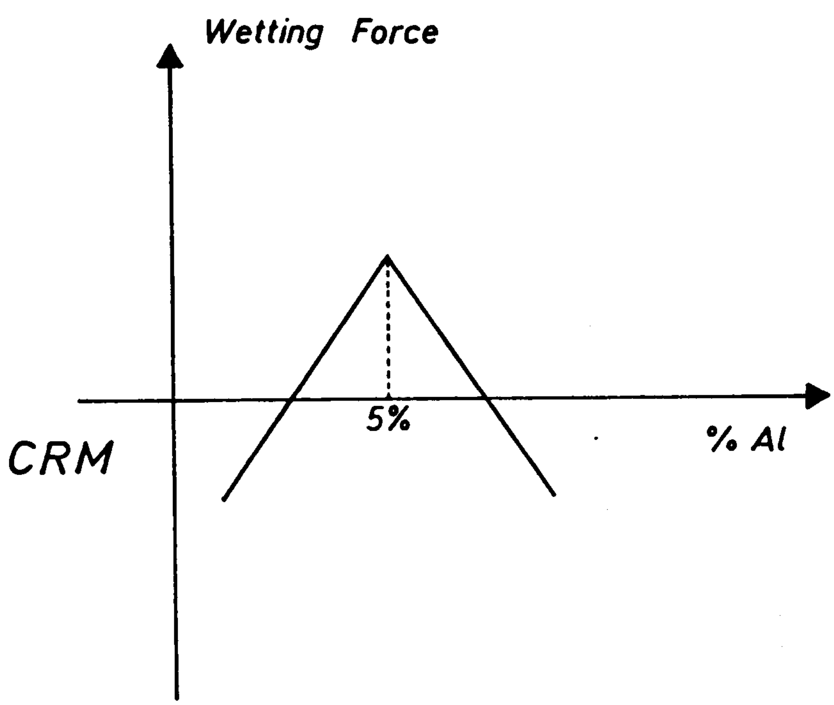

Weight
E
CRM
Time
E : Wetting Force


Wetting Force
CRM
Flux temperature


Wetting Force
T1
T2
T1 < T2
CRM
Iron contamination


Wetting Force
CRM
Flux density


Wetting Force
CRM
Galvanizing-
- temperature


Wetting Force
CRM
5%
% Al

PHENIX WORKS - RESULTS OF TWO-YEAR EXPOSURE PROGRAM

## GALFAN COILS CHARACTERISTICS

| Samples N° | Coils N° | Cooling rate * | Skinpass SKP Chromating Cr | Coating weight (gr/m2) (microns) |
|---|---|---|---|---|
| 1 | GALFAN Coil n°1 (I) | 1 | - | 125 (8 µ) |
| 2 | n°6 (I) | 2 (Heurtey Zn powder) | SKP | 260 (18 µ) |
| 3 | n°99 (II) | 1 | Cr | 375 (26 µ) |
| 4 | n°103 (II) | 2 à 4 | SKP | 235 (17 µ) |
| 5 | n°103R (II) | 2 à 4 | SKP + 30 Hrs/300°C | 235 (17 µ) |
| 6 | n°108 (II) | 2 à 4 | Cr | 310 (21 µ) |
| 7 | n°110 (II) | 4 à 5 | Cr | 330 (23 µ) |
| 8 | n°111 (II) | 2 à 4 | Cr | 260 (18 µ) |
| 0 | HDG | - | - | 275 (20 µ) |

1 = air cooling (regular spangle)
5 = fast cooling (>100°C/sec)

## GENERAL RESULTS

| Sample n° 1 | T° Bend Test | Impact Test | R x N 7,5 mm | Salt spray 1000 Hrs | Edge corrosion 750 Hrs | Edge corrosion 1000 Hrs |
|---|---|---|---|---|---|---|
| 1 | 1.7 | 10 | 7 | Good | D2/10 | D2/10 |
| 2 | 2.5 | 10 | 8 | Good | MD2/8 | D2/10 |
| 3 | 4.8 | 9 | 7 | Good | M4/6 | D2/8 |
| 4 | 2.5 | 9 | 7 | Good | M6/4 | MD4/6 |
| 5 | 2.6 | 9 | 7 | Good | MD6/5 | D2/10 |
| 6 | 4.0 | 9 | 7 | Good | D8/4 | D6/5 |
| 7 | 4.5 | 7 | 7 | Fail | * D6/5 | * D2/10 |
| 8 | 5.0 | 8 | 8 | - | - | - |
| 0 | 5.2 | 7 | 7 | Good | D6/5 | MD2/8 |

* Blistering F 8 on flat surface.

D= Dense
M= Medium

Numbers after slash
indicate mm of edge creep

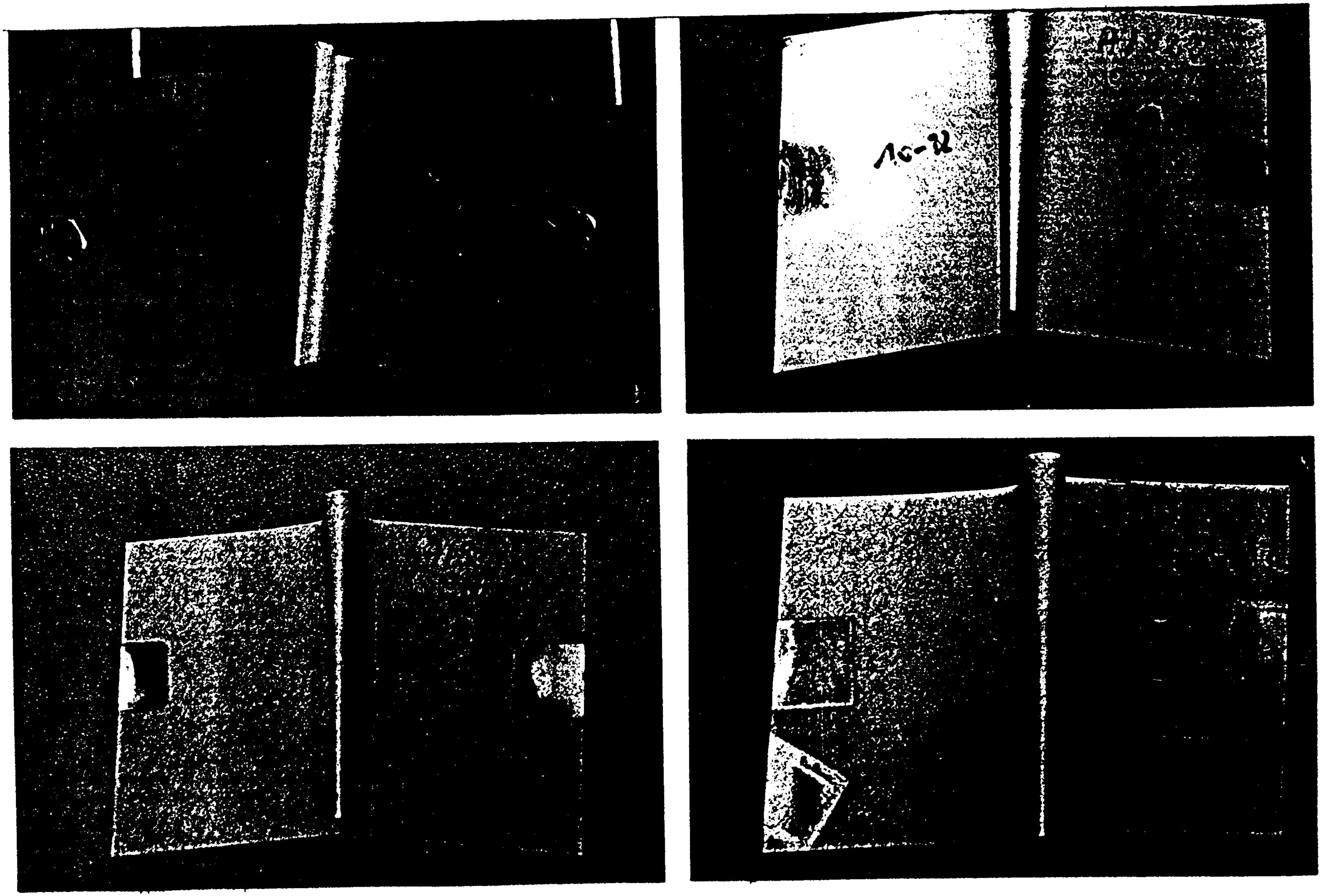
## OPERATING PRACTICE

| | | |
|---|---|---|
| Pretreatment : | PARCO 338 | - degreasing |
| | BONDERITE 1303 | - pretreatment |
| | PARCOLENE 62 | - chromate rinse. |
| Paint system : | PRIMER : epoxy type | - thickness 5 microns |
| | TOPCOAT : polyester | - thickness 20 microns. |

# 2 YEARS EXPOSURE OF COIL COATED GALFAN

MARINE    SEVERE MARINE

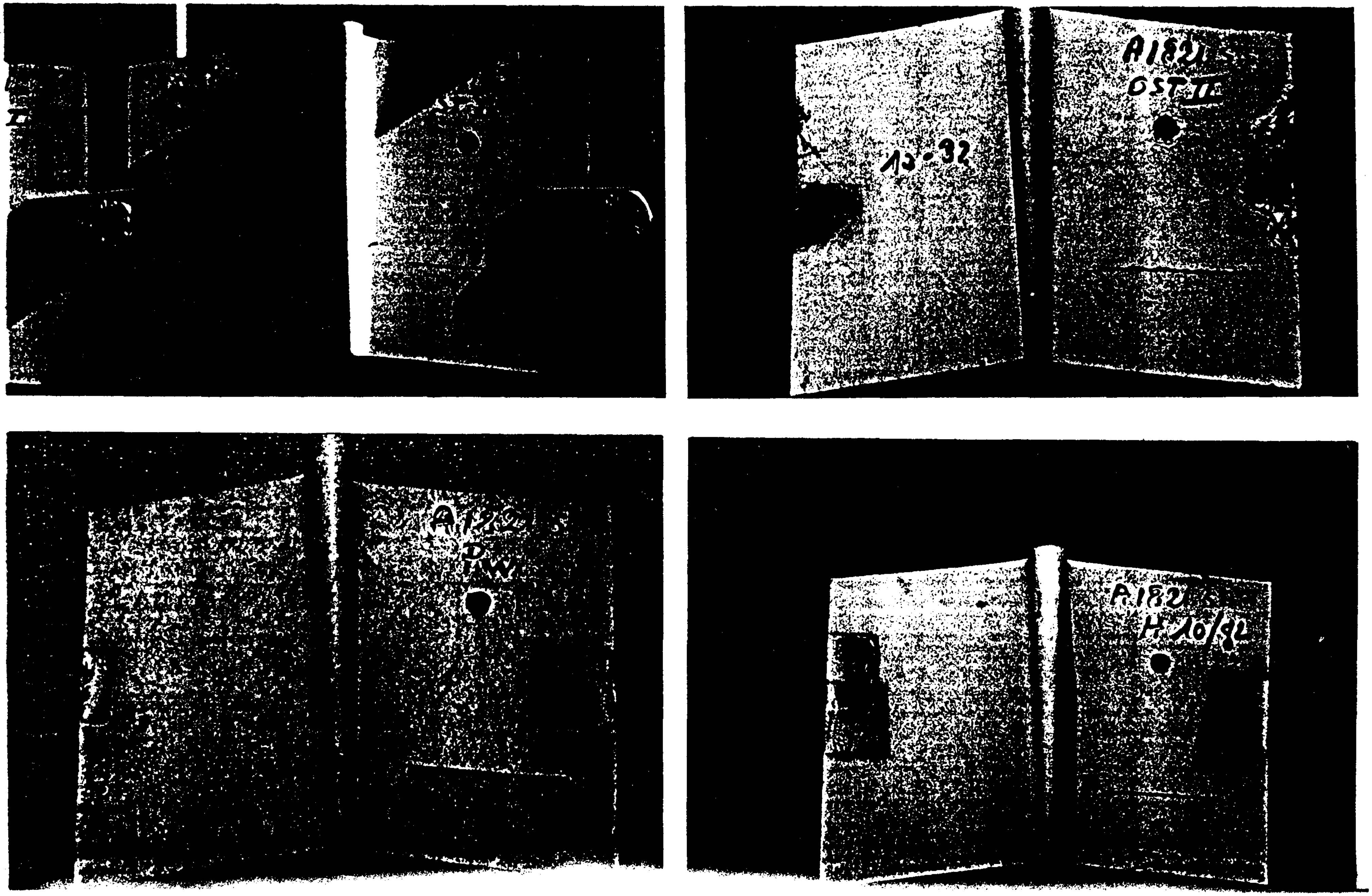
INDUSTRIAL    PLASTISOL    RURAL



# 2 YEARS EXPOSURE OF COIL COATED GALFAN

MARINE SEVERE MARINE

INDUSTRIAL POLYESTER RURAL



Note for the 7th Galfan Meeting, to be held on December 5, 1985.

# Influence of Aluminum Contents in Coating on the Properties of Galfan

by Yusuke Hirose, Nisshin Steel Co., Ltd.

In order to analyse the influence of aluminum contents in coating layer on the properties of Galfan, three different Zn-Al alloy coatings (4%Al-Zn alloy, 5%Al-Zn alloy and 7%Al-Zn alloy coating) have been investigated.

The specimens were produced by a 300mm pilot plant(NOF type CGL) using 0.5mm thick cold rolled steel strip, and they were subjected to the examinations such as metallographic test, corrosion test and so on.

The results are shown in Figure 1 through Figure 12.

Figure 1 Microstructure of the coating layers is different each other; the primary cristal in the 4%Al-Zn coating is zinc, 5%Al-Zn coating has almost the perfect eutectic structure and 7%Al-Zn coating has aluminum-rich phase as a primary crystal.

Figure 2 The microstructure of 4%Al-Zn coating becomes finer as the cooling rate after hot-dipping increases. Also the ratio of primary crystal to eutectic becomes higher.

Figure 3 Aluminum which is precipitated in the primary zinc becomes larger in quantity as the cooling rate increases.

Figure 4 Shrinkage grooves are produced at the coating surface. It is most notable on 5%Al-Zn coating.

Figure 5 The weight loss of 5%Al-Zn coating by white-rusting is larger than 4%Al-Zn or 7%Al-Zn coating.

Figure 6 The time to red-rusting of three Galfan coatings are approximately the same.

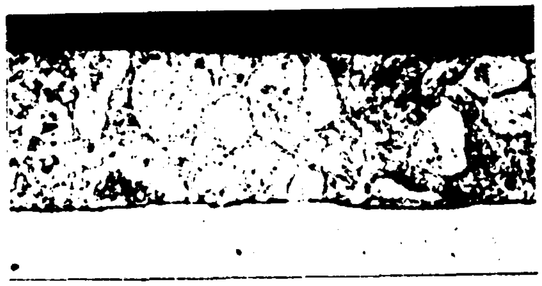
Figure 7- The specimens subjected to the corrosion tests show similar surface appearance regardless of aluminum contents.

Figure 9 The cooling rate does not substantially affect the corrosion resistance.

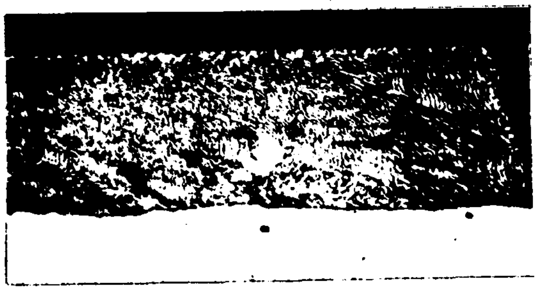
Figure 10-11 The formability of three coatings are basically the same, thus the corrosion resistance after forming shows the same performance.

Figure 12 The quantity of aluminum dissolved into the phosphating solution during phosphate treatment is largest on 7%Al-Zn coating.

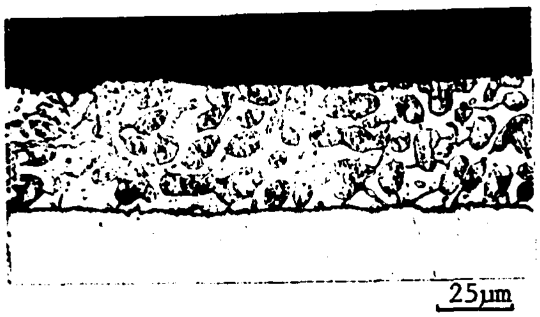
According to the above results, it is concluded that aluminum in the coating layer in the range of 4 to 7% does not have remarkable influence on their corrosion resistance and formability. Higher aluminum contents tend to obstruct the phosphatability due to the dissolved aluminum in the phosphating solution. 5%Al-Zn coating has poor surface appearance because of the grain boundary dent.



a) 4%Al-Zn

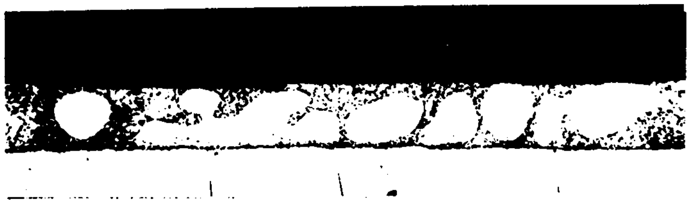


b) 5%Al-Zn

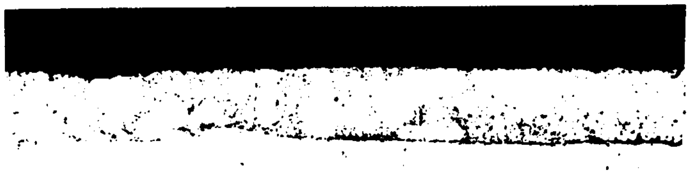



c) 7%Al-Zn

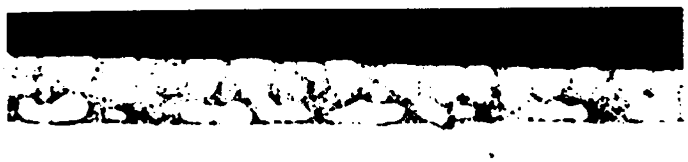
Figure 1 Microstructure of the coating layer



a) Cooling rate: 5°C/sec



b) Cooling rate: 20°C/sec

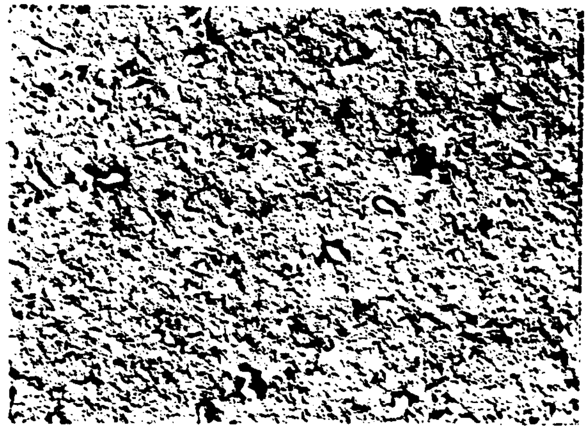


c) Cooling rate: 50°C/sec

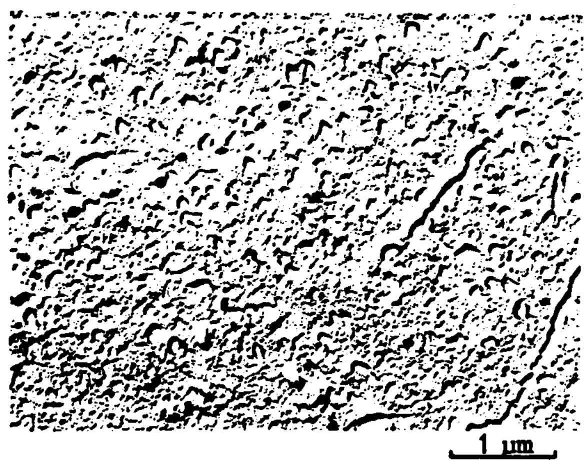
25μm

d) Cooling rate: 450°C/sec

Figure 2 Effects of cooling rate after hot-dipping on the microstructure of 4%Al-Zn coating



a) Cooling rate: 5°C/sec




b) Cooling rate: 50°C/sec

**Figure 3** Aluminum precipitated in the primary zinc crystal --- TEM images of the primary zinc in 4%Al-Zn coating

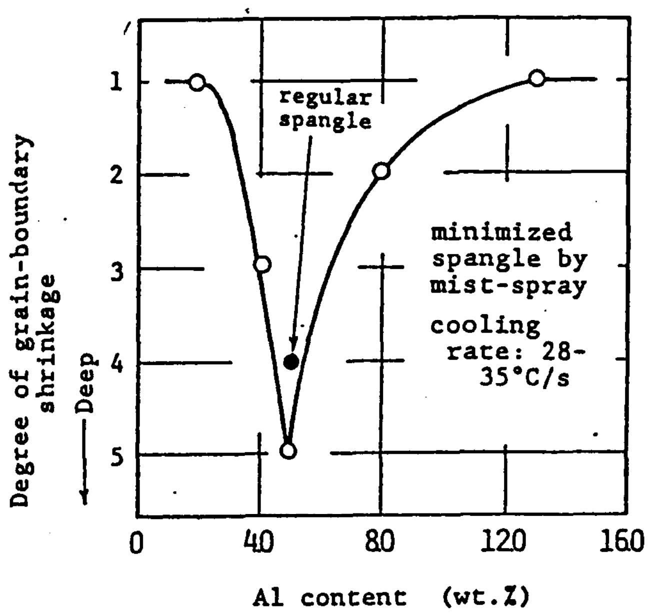



Figure 4 Relation between aluminum contents in the coating and the depth of grain boundary dent

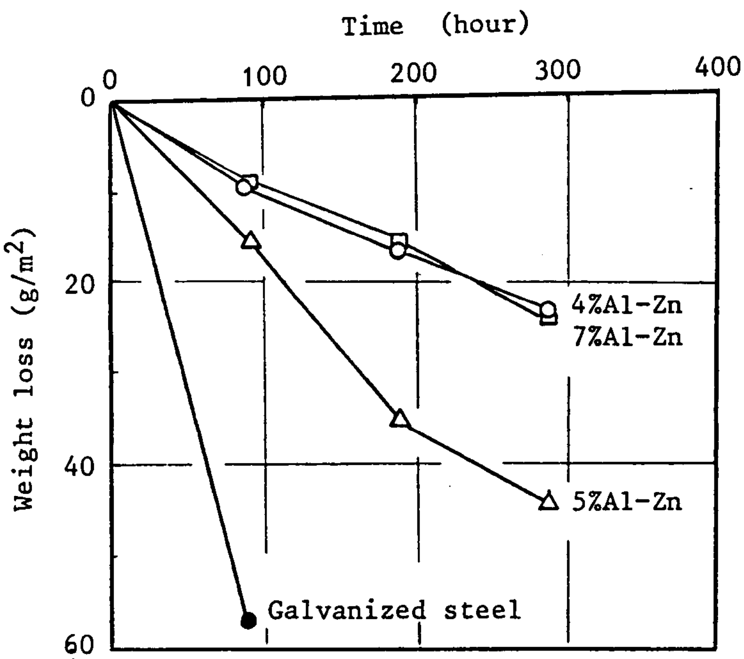



Figure 5 Weight loss of specimens due to white-rusting by salt spray test --- white-rust was removed by 3% acetic acid solution

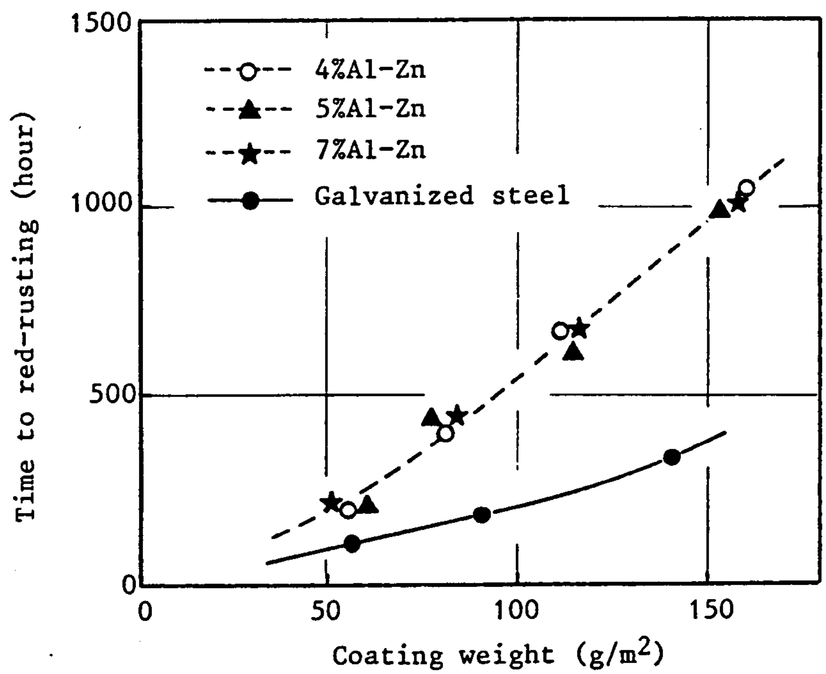



Figure 6   Time to red-rusting in salt spray test

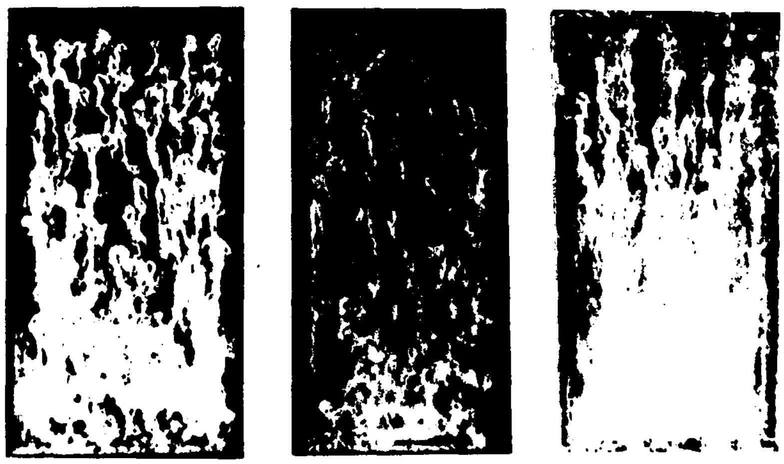



Figure 7 Appearance of specimens subjected to salt spray test for 1,000 hours

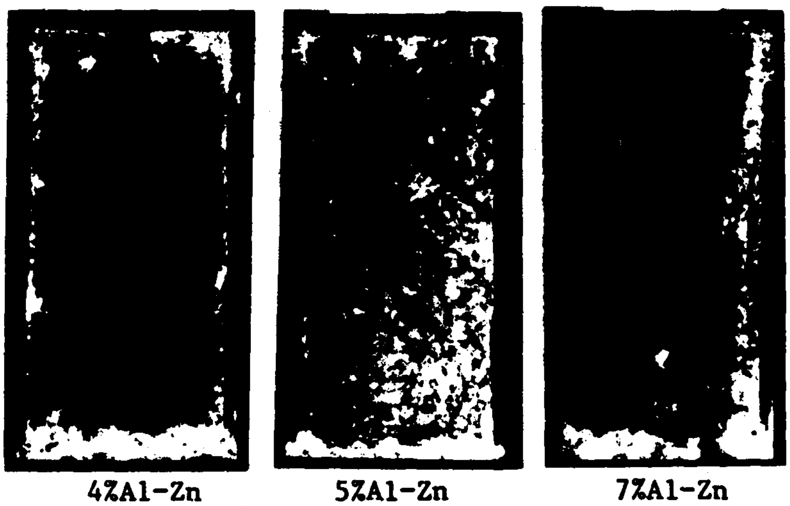



Figure 8 Appearance of specimens subjected to humidity cabinet test for 2,500 hours

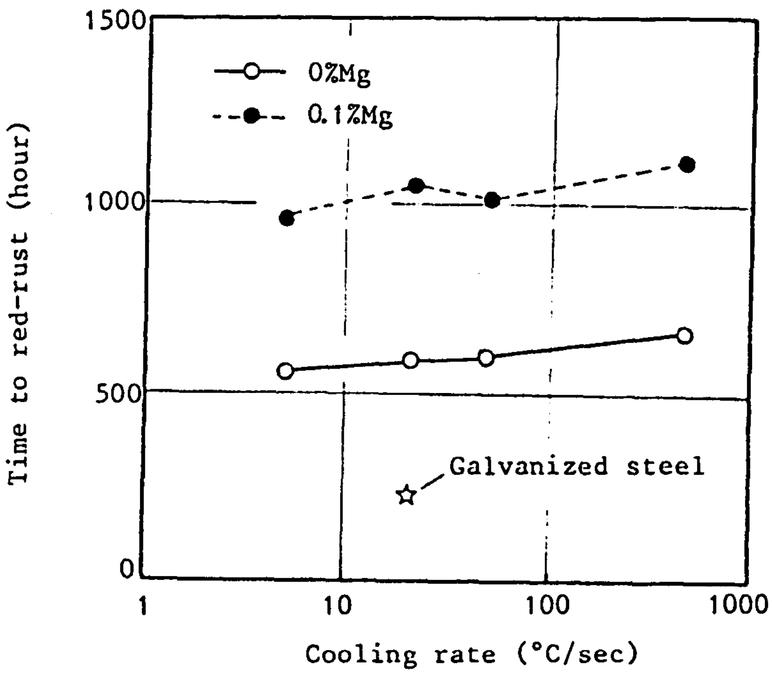
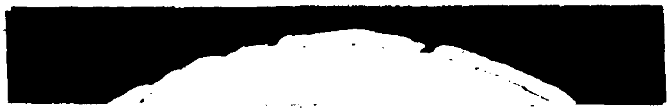
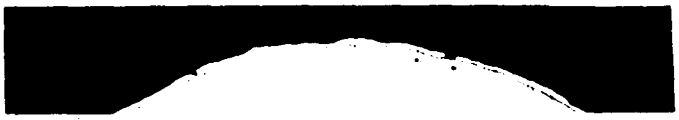


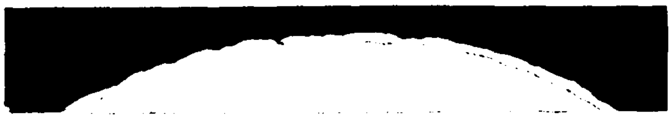

Figure 9 Influence of cooling rate on the corrosion resistance of 4%Al-Zn coating --- time to red-rust by salt spray test
(Coating weight: 90 g/m$^2$)



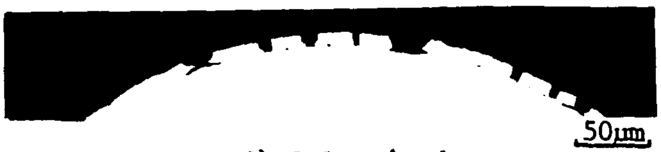
a) 4%Al-Zn



b) 5%Al-Zn

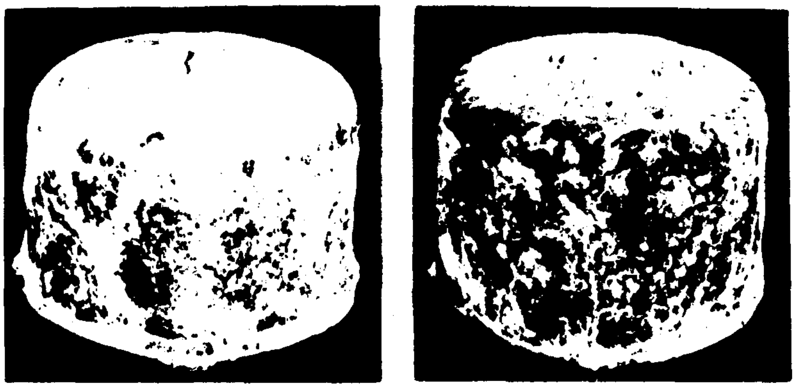


c) 7%Al-Zn




d) Galvanized

Figure 10 Cross-sectional structure of 2T-bended specimens



4%Al-Zn 7%Al-Zn

Figure 11 Appearance of cup-drawn specimens subjected to salt spray test for 500 hours

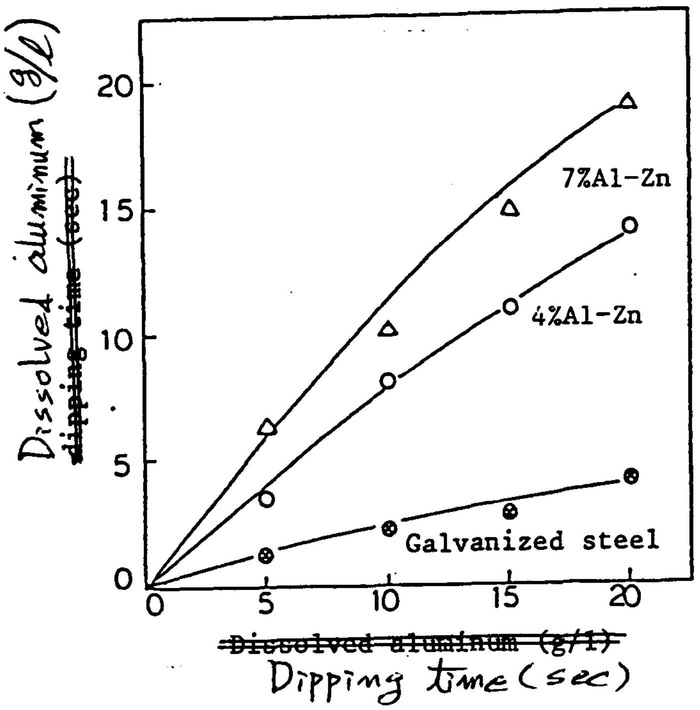



Figure 12 Quantity of dissolved aluminum in the phosphating solution

Hoesch Stahl

I would like to give you a short survey on the status of the GALFAN production and about the research activities of Hoesch Stahl AG.

We produce GALFAN on the galvanizing line of the plant in Eichen in campaigns of appr. 3,000 tons of GALFAN per campaign. At present the change of systems zinc/GALFAN /zinc is being made by pumping the melt. We dispose the zinc in a pot to keep the zinc-melt hot and we pour GALFAN to ingots and, therefore, we require 56 hours for this change-over, mainly due to the melting time of GALFAN.

In 1985, we have had three campaigns with production lots between 2,400 and 2,900 t, so that the total production at Hoesch amounts to 13,400 tons.

With all productions we had an amount of dross of 1.6 kg/t on an average as compared to galvanized, where we had between 3 to 4 kgs dross per ton produced.

We produce all qualities known in galvanizing, i.e.

Lockformer Quality
Lockformer skinpassed on-line
Drawing Quality
Special Drawing Quality (I-F Steel)

Thickness varies from 0.6 to 3.0 mm. The speed of the line is 30 to 130 m/min. The temperature of the bath varies from 430 to 470°C. The temperature of the submerging steel sheet is 465 to 530°C.

From the analysis you can see that the aluminum content of the ingots has been a little bit low.

The concentration of Cer and Lanthanum has been exactly determined. The lead content in the bath is slightly increased. It did not, however, as later tests showed, lead to inter-crystalline corrosion.

It is notable, and this confirms earlier tests, that aluminum, cerium and lanthanum concentrate in the top dross. Especially cerium and lanthanum are hardly found in the coating layer.

During production, we experience great difficulties, especially with a view to a uniform good surface. Hereinafter I can give you some examples for such difficulties:

1. The cleanliness of the cold rolled material. We have found that the cleanliness of the cold rolled material is of utmost importance.

2. The influence of the nozzles, the air pressure and the medium (air or nitrogen). We have found that when using air, the result becomes worse with increased pressure. When using nitrogen -we have carried out a short test - the results are considerably better with a view to the quality of the surface.

The cooling after coating is of importance for the compound of the layer, you can see this from the available photos.

We have taken microsections of samples which had not been quenched by water-air and of samples which had been quenched very heavily. You can see that with unquenched GALFAN sheet the (denatritically shaped) primary crystals are mostly near the surface of the steel and move from there into the coating. This points out that the liquid coating begins to stiffen at the surface of the steel sheet.

With a more intensivewater -quenching the primary crystallization occurs more at the surface of the coating. When checking the results we found a phenomenon, we cannot fully explain until now. A homogeneous zinc-aluminum-melt with an Al-content of 4.98 % - as given in our case- should crystallize eutectially. However, the coating of the tested coils shows clearly a high portion of primary $\alpha$ mixed crystals. The crystallization taken from the Zn-Al-balance are, obviously not transferrable to the crystallization of the GALFAN coating.* Here still has to be carried out some more research work.

* We have found a dependence between thickness of the strip and the amount of $\alpha$-crystals in the layer.

## Soldering and Welding Technique

We work in our lab for welding technology at present to find the best conditions for soldering and welding of GALFAN. Partial results for soldering with a bit have been obtained already. One arrives at good results when using a commercial soft soldering means, as described in DIN 1707, Table 1, Group A. The chemical compound is for instance zinc (60%), Antimony (0.12-0.5%), and lead balance.

The selection of an appropriate fluxing material is of importance. We found out that a fluxing means as per DIN 8511 of the group F-SW 12 or F-SW11 is suitable with a chemical compound of zinc (10%), Bortrioxid ($B_2O_3$) (13%) and Ammonium with a portion of 23%.

All other tests in this field have not been completed yet, so that we cannot make any statements in this respect.

I have indicated with examples and some figures that Hoesch Stahl AG is willing to produce GALFAN to a larger extent and introduce it to the market. We have to overcome considerable problems, in order to meet all requirements of the product.

However, we believe that these problems can be solved and that we can offer with GALFAN a product, that has many advantages and will certainly be accepted by the customers more and more in the future.

Thank you.

# GALFAN

HOESCH-PRODUCTION

EICHEN WORK

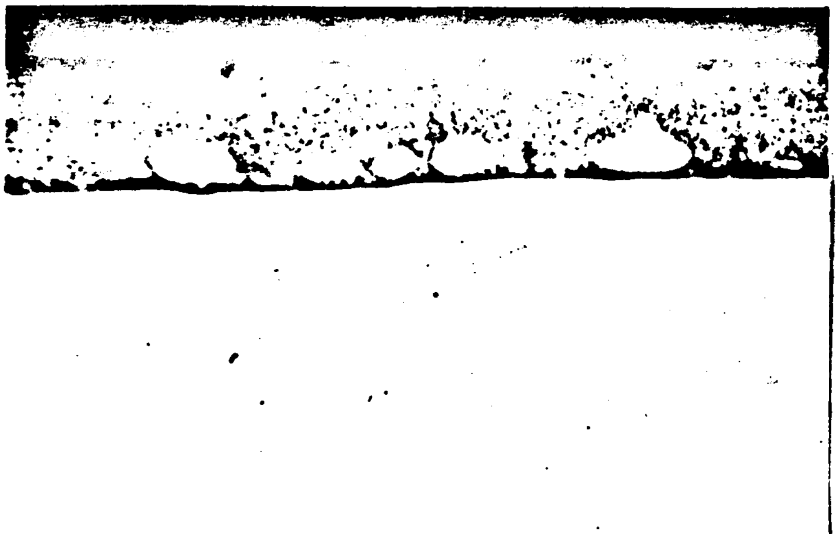
| | |
|---|---|
| MARCH 1985 | 2900 to |
| JULY 1985 | 2720 to |
| OCTOBER 1985 | 2400 to |
| TOTAL PRODUCTION 1984/85 | 13800 to |
| INGOT WEIGHT | 2 to |
| DROSS | 1,6 KG/to PROD. |

## produktion items

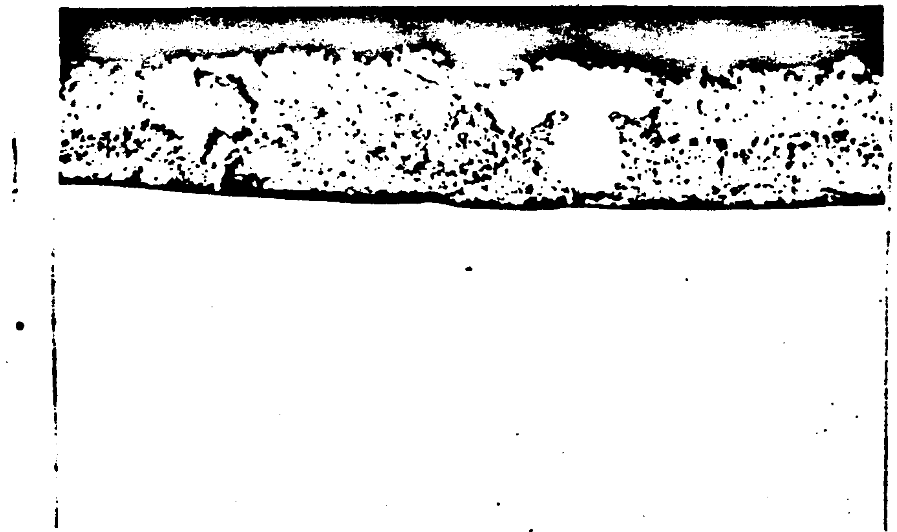
| | |
|---|---|
| Quality | Lockformer Quality<br>Lockformer skinpassed on-line<br>Drawing Quality<br>Special Drawing Quality (I-F Steel) |
| Thicknes | 0,6 - 3,0 mm |
| Speed | 30 - 130 m/min |
| Temperatur | |
| bath | 430 - 470 °C |
| strip | 465 - 530 °C |

Analysis (%)

| | | ingots | bath | dross | layer |
|---|---|---|---|---|---|
| Al | | | | | |
| | $\bar{x}$ | 4,77 | 4,92 | 8,70 | 4,81 |
| | $\pm$ S | 0,07 | 0,14 | 2,25 | 0,10 |
| | N | 3 | 18 | 19 | 88 |
| Pb | | | | | |
| | $\bar{x}$ | 0,013 | 0,0039 | 0,0053 | 0,0062 |
| | $\pm$ S | 0,0006 | 0,0014 | 0,0016 | 0,0017 |
| | N | 3 | 18 | 19 | 82 |
| Ce | | | | | |
| | $\bar{x}$ | 0,023 | 0,0058 | 0,057 | 0,0048 |
| | $\pm$ S | 0,001 | 0,0032 | 0,004 | 0,0009 |
| | N | 3 | 22 | 19 | 44 |
| La | | | | | |
| | $\bar{x}$ | 0,020 | 0,0037 | 0,052 | 0,0027 |
| | $\pm$ S | 0,0015 | 0,0042 | 0,005 | 0,0005 |
| | N | 3 | 22 | 19 | 44 |

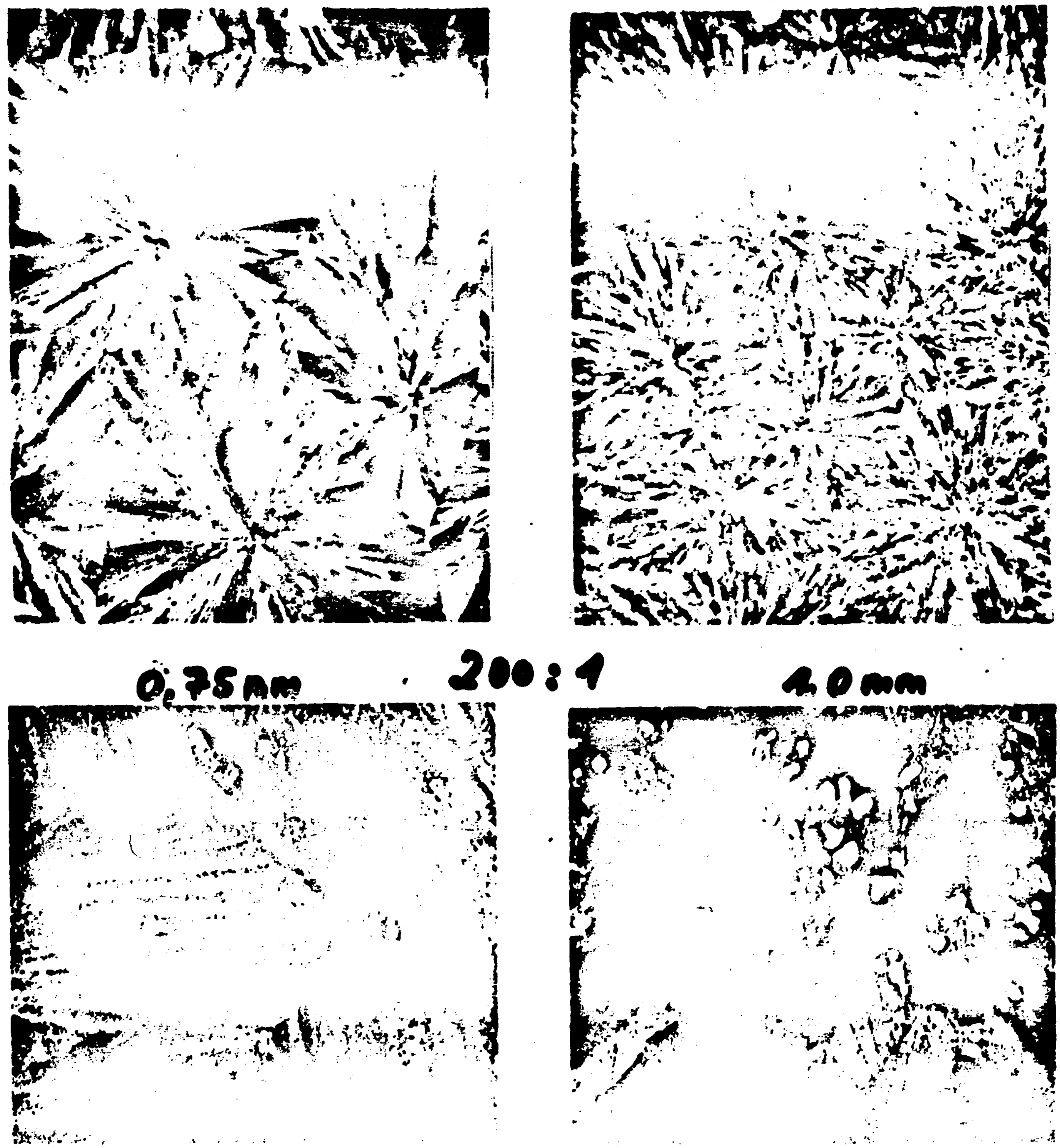


Normal cooling

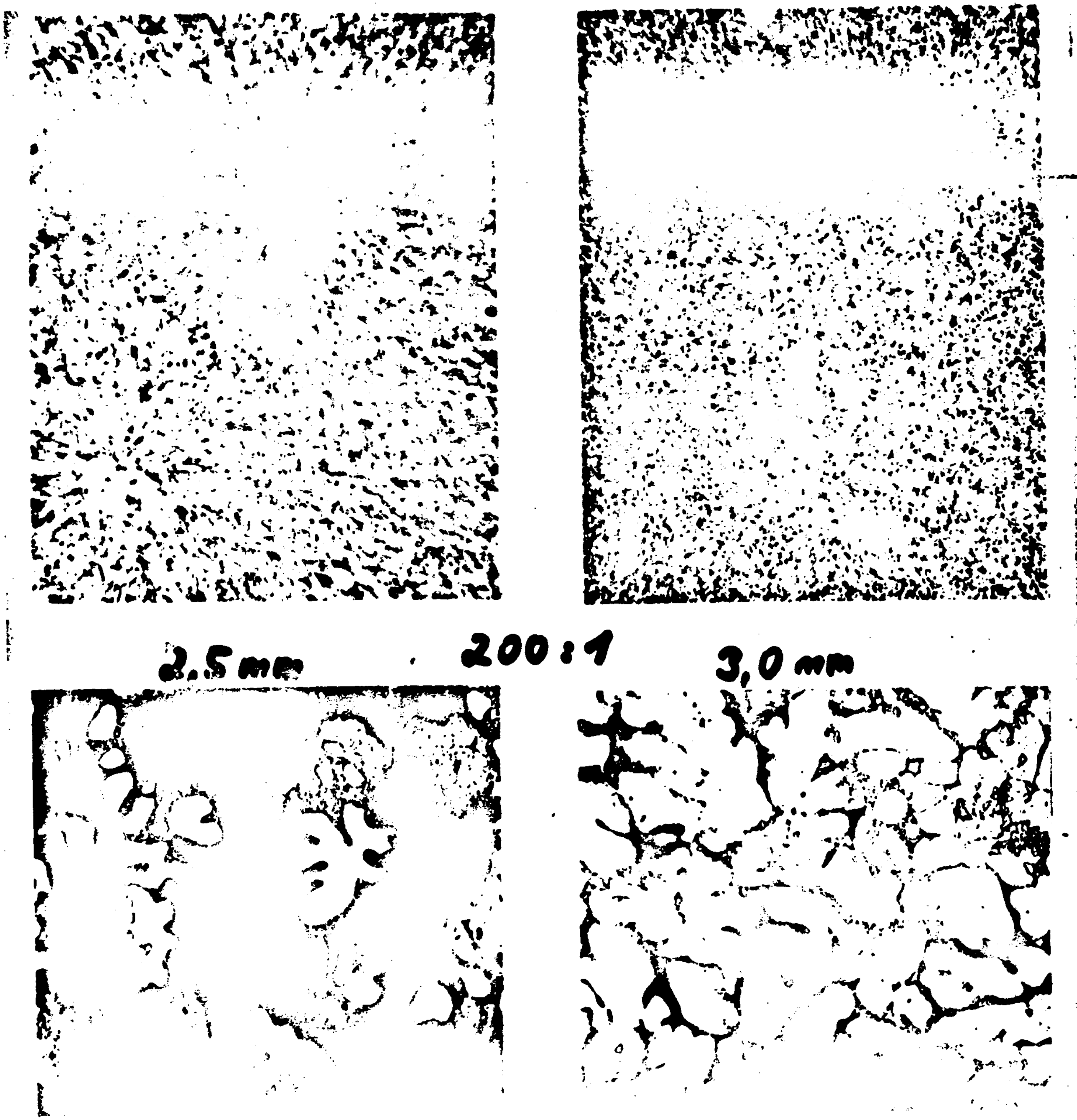


vaporized water cooling

1019



16:1



200:1

2,5 mm 3,0 mm

| Soft solder | Chem. Analysis | | | ~~DIN 1707~~ |
|---|---|---|---|---|
| | Sn | Sb | Pb | DIN 1707 |
| | 59,5 - 60,5 | 0,12 - 0,5 | Balance | L - Sn 60 Pb (Sb)<br>Tabelle 1, Gruppe A |
| fluxing agent | Zn | $B_2$ $O_3$ | $NH_4$ | DIN 8511 |
| | 10,0 | 12,8 | 23,4 | F-SW12 oder F-SW11<br>(residues carefully to be removed) |

**FABRIQUE DE FER DE MAUBEUGE** LOUVROIL, le DECEMBRE 1985

REUNION GALFAN DE DECEMBRE 1985

I/ - PRODUCTION RUNS : To date the FFM have produce more than twenty thousand tonnes of GALFAN. The main remark we notice about this product is its sensitivity to running parameters and the importance of the strip quality.

a) Bright Surface : We have to use strip without defects (scales, scratches) because they are visible under a such coating.

b) Bare spots : concerning the annealing furnace it's necessery to check all the parameters to reduce the oxydes present on the strip. We think that's the main cause of bare spot formation.

c) Uncovered areas : The wiping system can create important troubles when pressure and flow conditions aren't ajusted. The air wiping knifes may remove some zinc especialy for thin gages and light coatings.

d) Flux lines : At last it seems that bottom drosses arises easily on the coating surface and cause somes troubles.

2/ SOIL CORROSION RESISTANCE : To compare traditionnel galvanized coating and GALFAN, differents samples have been buried in two soils maintained at PH 4 and 8. The corrosion evaluation is done by a comparison between measures of weight loss and zinc coating weight.

In any cases, the results show less corrosion for GALFAN profiles.

The corrosion resistance improvement is higher in lemestone, a basic soils.

## III/ PRODUCT EVALUATION :

a) Smoothness :

Our GALVALISS is a strip galvanized and wiped by nitogen finishing. For light coatings, the surface is very regular and ultrasmooth.

b) Salt spray test : (5% red rust)

For medium coating weight ( Z 225 ) the performances are : 400 hours for usual Galfan and about 2000 hours for polyester coated GALFAN.

c) Plastisol coating adhesion :

For plastisol coating Galfan the immersion test in boiled water on a erichsen drawing (7 mm) give good results during 4 hours.

This examples show versatility in GALFAN using

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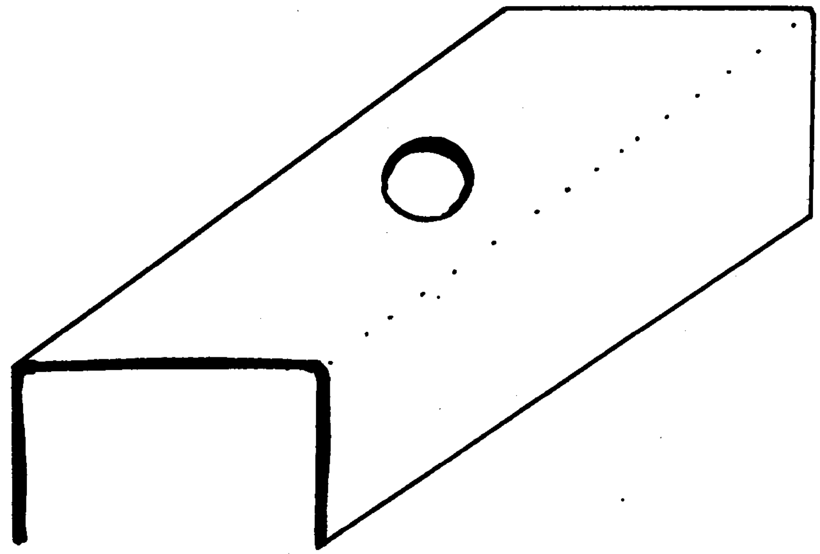

| "schiste" ph=4 | weight | loss |
|---|---|---|
| Galva | 1,4 g | 25% |
| Galfan | 0,9 | 16% |
| "limon" ph=8 | | |
| Galva | 2.2 | 40% |
| Galfan | 1 | 18% |

FFM

# RUN PARAMETERS

| | | | | | |
|---|---|---|---|---|---|
| STRIP | THICKNESS | : | 0,5 | - | 2 mm |
| | WIDTH | : | 800 | - | 1250 mm |
| | SPEED | : | 40 | - | 95 m/mn |

| | | |
|---|---|---|
| COATINGS | Z 90 | 13 % |
| | Z 100 | 20 % |
| | Z 150 | 7 % |
| | Z 225 | 3 % |
| | Z 275 | 54 % |
| | Z 350 | 3 % |

PREHEATER TEMPERATURE : 1200 °C

ULTIMATE STRIP TEMPERATURE : 780 °C

STRIP TEMPERATURE ENTERING THE BATH : 480 °C

BATH TEMPERATURE : 440 °C

BATH ANALYSIS : Al = 4,8 %

La = 0,02

Ce = 0,04

Pb = 0,003

BOTTOM DROSSES ANALYSIS

Al = 4,5 %

Fe = 0,4

Ce = 2

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# Coating Conditions to Get the Uniform Microstructure

December 5, 1985

KAWASAKI STEEL CORPORATION

For presentation at 7th Galfan Licensees
Meeting held in Brussels

## 1. Introduction

The microstructure of Galfan coating affects its corrosion behaviors. The precipitation of the Zn-rich primary phase in the microstructure deteriorates the corrosion resistance. The best resistance can be obtained when the microstructure is uniform, eutectic structure. In the previous report [1)] the influence of bath compositions (Al content) and cooling rates after coating on the microstructure were investigated. The uniform microstructure is obtained when Al content is 5.2~5.4% which is slightly above the eutectic composition in Hansen's phasediagram [2)], and /or when the specimen is cooled as rapidly as quenching into water bath. Recently, it has been confirmed that there are other factors which have to be controlled to obtain the uniform structure. For instance bath temperatures, immersion temperatures of sheets, and other factors may affect the microstructure significantly. In this paper the influences of the bath temperature and the immersing steel sheet temperature on the microstructures of the coatings were mainly investigated, and the corrosion behavior of Galfan coating was also discussed.

## 2. Experimental procedure

### 2.1 Laboratory experiments

A low C Al-killed cold rolled steel sheet (thickness 0.7mm) was subjected to experiments. The steel sheet was sheared into test specimens (40mm×150mm) and degreased. The specimens were, then, annealed and coated with Zn-5%Al alloy in a vertical galvanizing furnace in our laboratory. Bath temperatures and immersion temperatures were varied from

420°C to 500°C and from 440°C to 660°C, respectively. The heat cycles and coating conditions are shown in Table 1.

2.2 Experiment in CGL (continuous galvanizing line)

A low C Al-killed cold rolled steel sheet (thickness 0.5mm) was coated in CGL at Chiba works of KAWATETSU GALVANIZING COMPANY. The bath temperatures were 460°C and 500°C and the immersion temperatures were varied from 480°C to 660°C. The Galfan coated specimens were subjected to a formability test (0T bending) and a salt spray test. The coating conditions are shown in Table 2.

3. Results and discussion

3.1 Temperatures of the bath and the immersing steel (laboratory experiments)

Crossectional microstructures of coatings are shown in Photo. 1. When the bath temperatures were 420°C and 460°C, the microstructures of coatings were uniform without precipitation of Zn-rich primary phase independently of immersion temperature between 440°C and 660°C. When the specimens were dipped into a high temperature bath (500°C), Zn-rich primary phase (white color phase in Photo. 1) precipitated.

Crosssectional microstructures of the coated specimens by scanning electron microscopy (SEM) are shown in Photo. 2. In the Photo. β-Zn and α-Al phase are appeared to be bright and dark color, respectively. The interfacial layer between the base steel and the coated layer became thicker as bath temperature was higher. Immersion temperature, however, little influenced on the thickness of the interfacial layer.

Characteristic secondary electron beam images were obtained on the crossections of the specimen. The images shown in Photo. 3 were specimens dipped at 600°C into bath of 500°C for 30 sec. The reactions between coating metal and steel proceed so extremely in such conditions that the coating was separated into two layers, Zn-rich surface layer and Al-rich intermediate one.

The above results indicate that the reactions between melting metal and steel are more active and intermetalic compounds are more easily formed at the interface as bath temerature is increased. Al in a bath reacts with steel more easily than Zn and Al is concentrated in the interfacial layer. Amount of Al near the base steel decreases and is less than eutectic composition, so that primary phase easily precipitates.

In hot dip coating dissolution of Fe into bath from steel sheet is inevitable, so coating alloy consists of three elements, Zn, Al and Fe. Amount of Fe dissolution increases with the bath temperature. This may be another reason to produce the Zn-rich primary phase in the coating when bath temperature becomes high.

### 3.2 Properties of Galfan coated in CGL

#### 3.2.1 Microstructure

Microstructures of the specimens coated in CGL are shown in Photo. 4. When the bath temperature was 460°C, primary phase rarely precipitated and the coatings were uniform. On the other hand, Zn-rich primary phase precipitated in the coating when the bath temperature was 500°C. The change in immersion temperature of strip little influenced on the microstructure. This result corresponded to the result in the laboratory.

3.2.2 Formability

Surface appearances at the deformed part in the 0T bending test are shown in Photo. 5. In all specimens cracks were observed on the coating surface. Especially the specimen coated in the bath of 500°C was damaged from many cracks. The best formability inhered in the specimen dipped into 460°C bath at 480°C of immersion temperature.

3.2.3. Corrosion behavior

Weight losses of the coating in the salt spray test are shown in Fig. 1. The bath temperatures and the immersion temperatures of strip were 460°C and 560°C in Galfan 3, 500°C and 650°C in Galfan 5, respectively. The microstructure of Galfan 3 had uniform eutectic phase and Galfan 5 consisted of eutectic and primary phase. Both Galfans showed better corrosion resistance than galvanized steel (GI). The weight loss in Galfan 3 was the smallest and showed the best corrosion resistance.

Microstructures of the coatings after the salt spray test are shown in Photo. 6. The specimen of the uniform eutectic structure corroded uniformly from the surface. (A) In the presence of the primary phase the boundary with the eutectic phase selectively corroded. (B) It is known that Al-rich phase exists at the boundary. Al-rich phase at the boundary deeply corrods at first and then corrosion proceeds to whole coating layer. Consequently the corrosion resistance of uniform microstructure is better than duplex microstructure of primary and eutectic phase. The selective corrosion was also observed in painted specimens. Since the corrosion solution turned alkaline under the painted film, the eutectic phase, which contained more Al than primary phase, selectively corroded. It is supposed that the solution turns alkaline at the boundary in unpainted specimens, and that Al-rich phase at this portion is initially attacked.

3.2.4 Surface appearance

Many craters and bare spots were observed in the specimens coated in the bath of 460°C. The influence of immersion temperature of strip on the number of craters is shown in Fig. 2. As the immersion temperature rose higher, the number of craters decreased.

It is supposed that poor wettability between melting metal and steel sheet and/or dross blown off by gas wiping caused crater. In order to improve wettability and to prevent crater it was effective to let immersion temperature higher. The coating with uniform microstructure and good surface appearance was obtained when the bath temperature was kept at 460°C and the immersion temperature was higher than 550°C.

## 4. Conclusion

The coating conditions to get the uniform microstructure were investigated. The results are summarized as follows.

1) Bath temperature influenced on the microstructure of Galfan coating, however, immersion temperature of specimen little influenced. When the bath temperature was 460°C, the microstructure of the coating layer was uniform. Zn-rich primary phase precipitated when the bath temperature was 500°C.

2) The boundary between eutectic and primary phase corroded selectively. The uniform microstructure showed better corrosion resistance than the duplex structure including primary phase.

## References

1) A. Yasuda et al. : "Microstructure of Zn-Al Alloy Coating", Note for the 5th Galfan Licensees Technical Meeting (1984)

2) M. Hansen : Constitution of Binary Alloys (1958) p148

Table 1 Coating conditions in laboratory

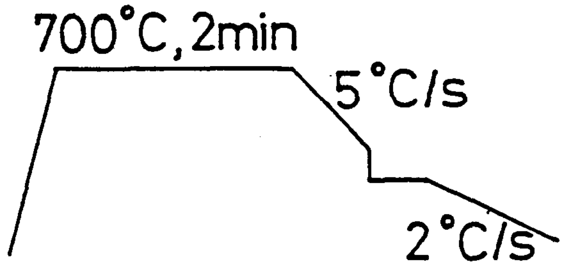
| | |
|---|---|
| Bath composition | 5.3%Al - Zn |
| Bath temperature | 420 460 500 °C |
| Immersion temp. | 440 ~ 660 °C |
| Immersion time | 10 (30) sec |
| Heat cycle | <br>15%$H_2$+ 85%$N_2$ |

Table 2 Coating conditions in CGL

| No. | Bath temp. (°C) | Immersion temp. (°C) | Bath composition | | | Coating weight (g/m2) |
|---|---|---|---|---|---|---|
| | | | Al | Fe | Pb | |
| 1 | 460 | 480 | wt% 5.63 | 0.04 | 0.002 | 103 |
| 2 | | 520 | | | | 121 |
| 3 | | 560 | | | | 119 |
| 4 | | 660 | | | | 117 |
| 5 | 500 | 650 | 5.5 | 0.02 | 0.003 | 135 |

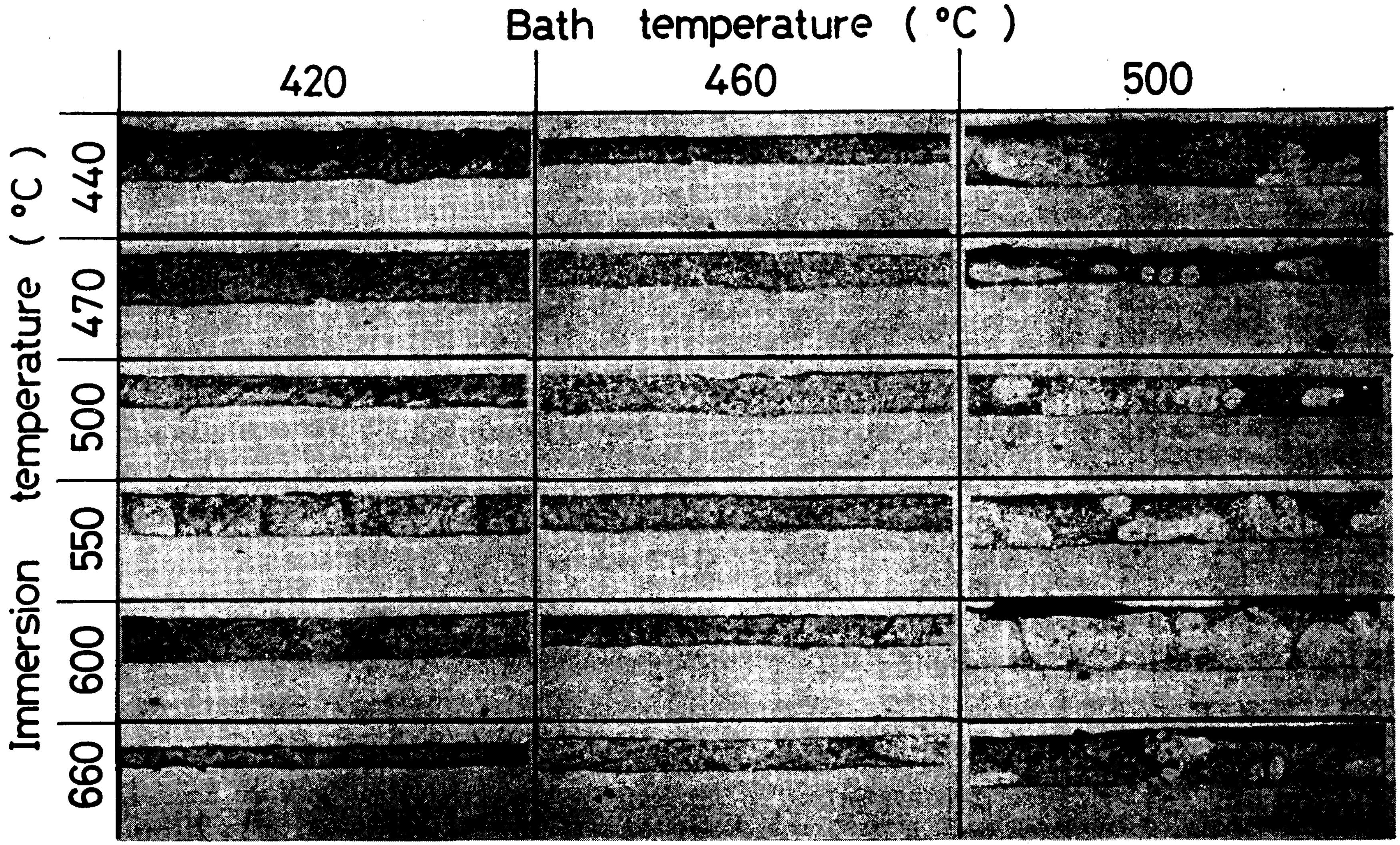



Photo. 1 Crosssectional microstructures of specimens in the laboratory.

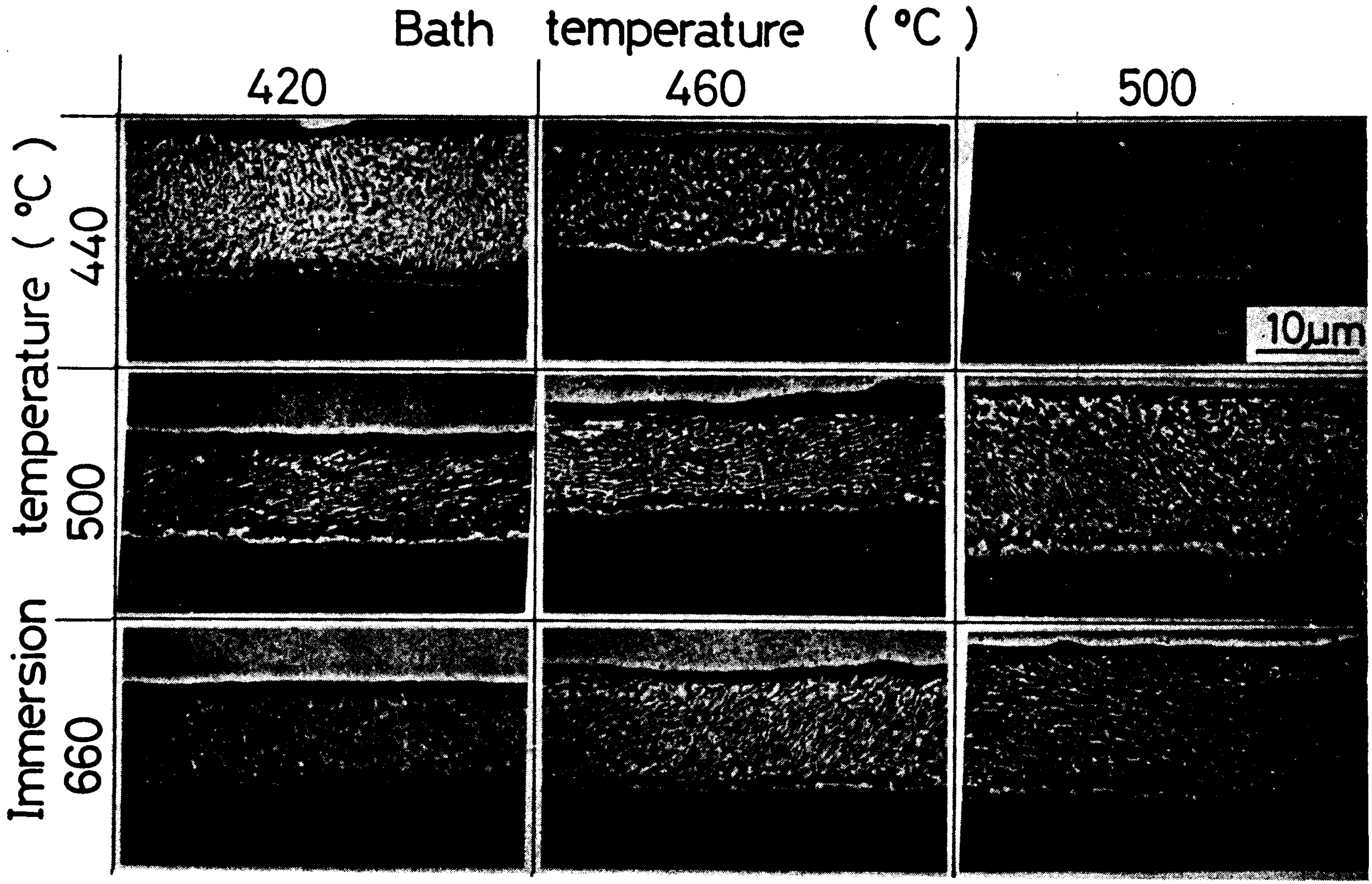



Photo. 2 Crosssectional microstructures by scanning electron microscopy.

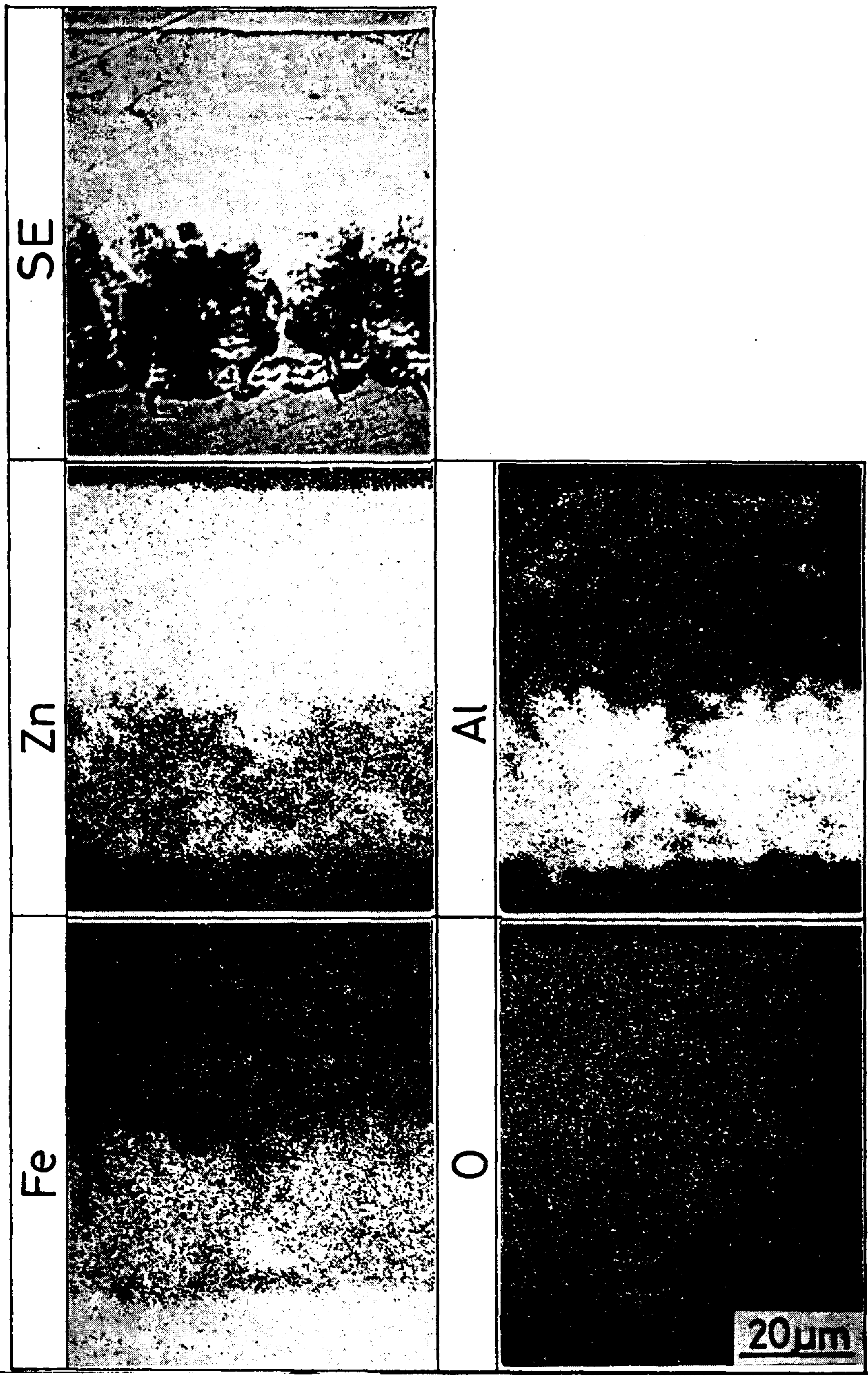



Photo. 3 Characteristic secondary electron beam images of crosssection.
( bath temp. 500°C, immersion temp. 600°C immersion time 30 s )

| | Bath temp. | Immer. temp. |
|---|---|---|
| 1 | 460 °C | 480 °C |
| 2 | 460 °C | 520 |
| 3 | 460 °C | 560 |
| 4 | 460 °C | 660 |
| 5 | 500 | 650 |

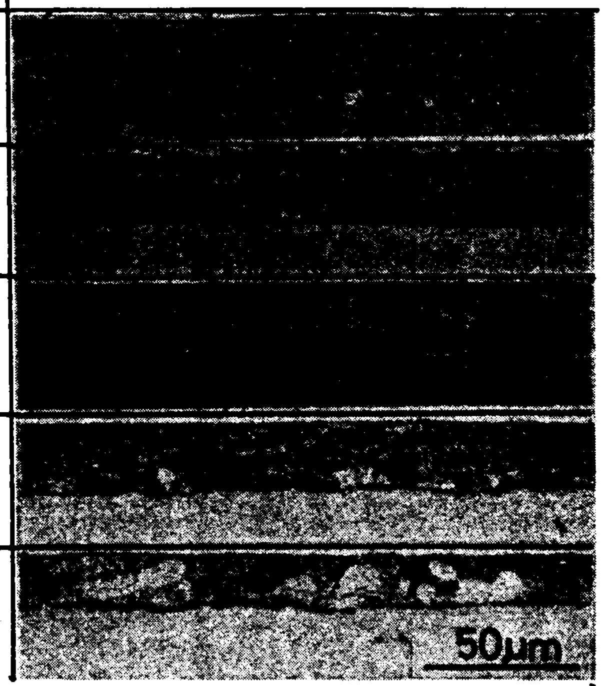



Photo.4 Crosssectional microstructures of specimens in CGL

| | Bath temp. | Immer. temp. |
|---|---|---|
| 1 | 460 °C | 480 °C |
| 2 | | 520 |
| 3 | | 560 |
| 4 | | 660 |
| 5 | 500 | 650 |

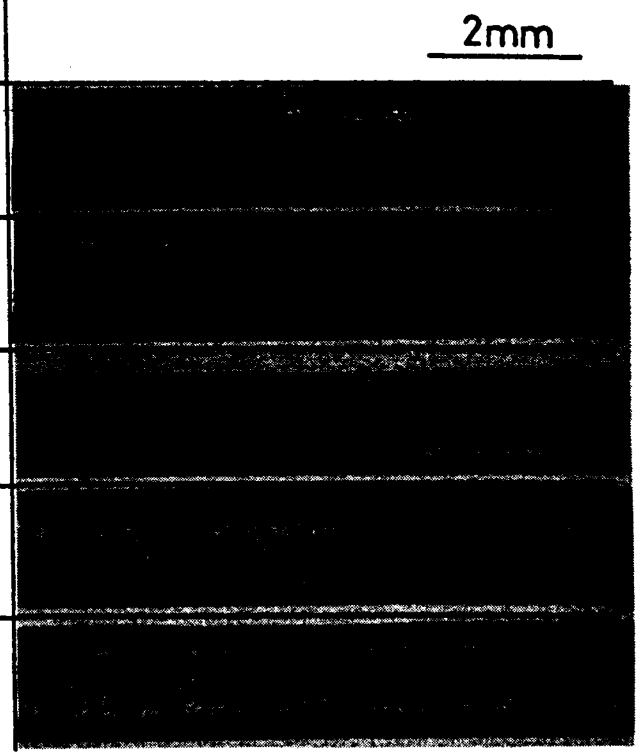



Photo.5 Surface appearances of bend portion ( OT bend )

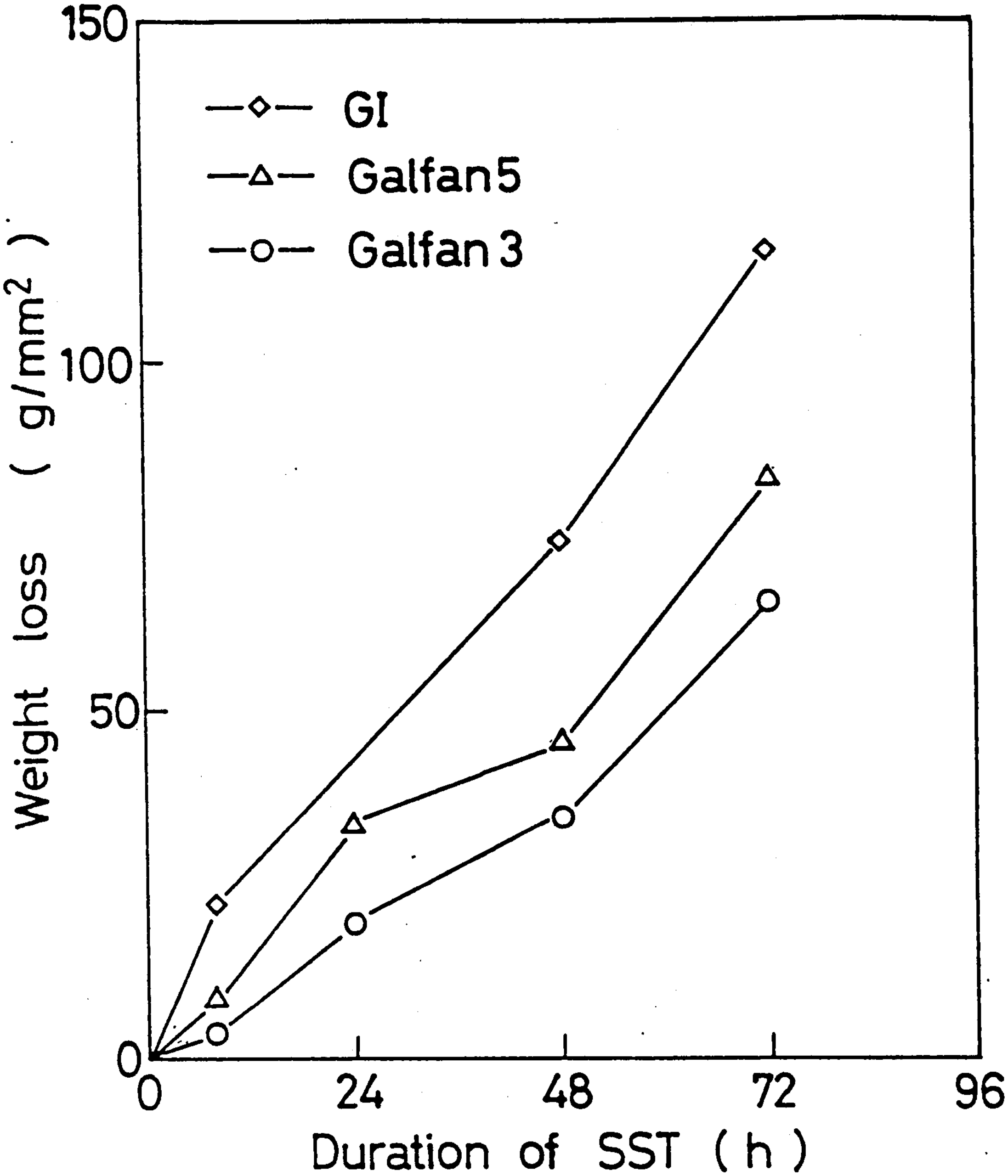
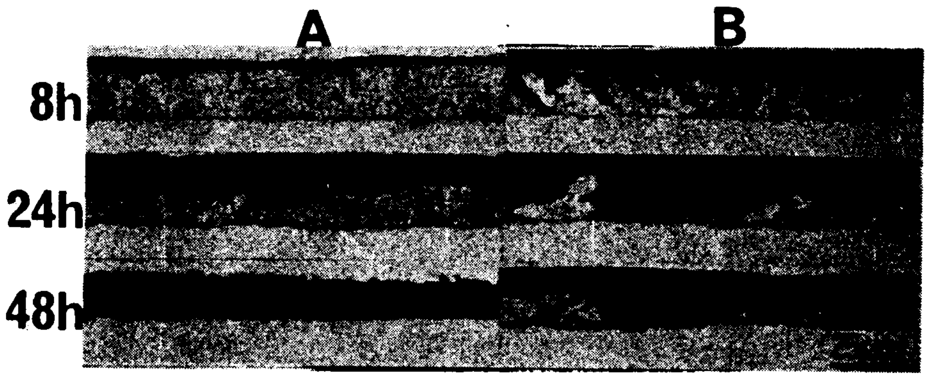



Fig.1 Weight loss of specimens after the SST




A Uniform structure
B Duplex structure

Photo. 6 Crosssectional microstructures of specimens after the SST.

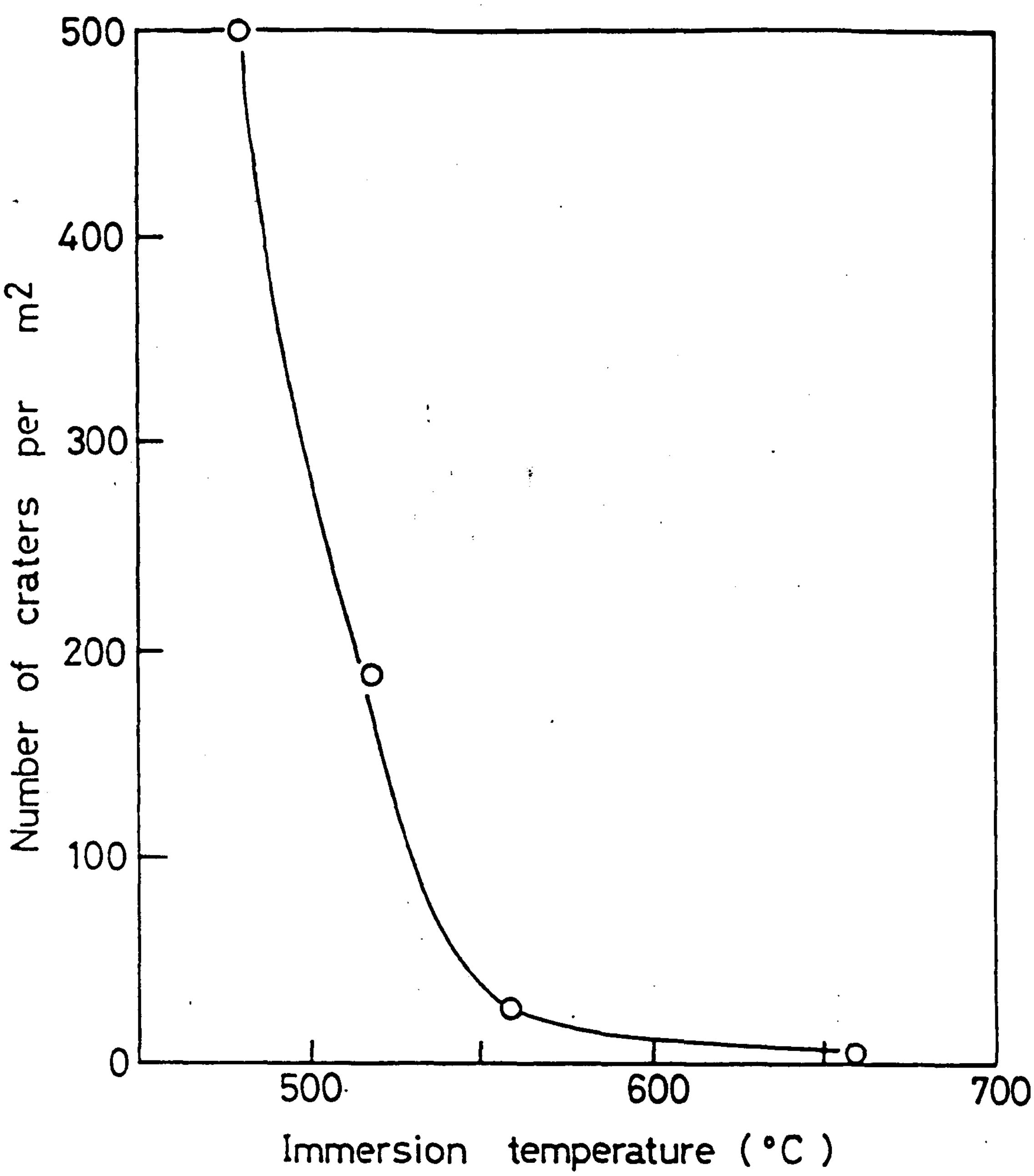



Fig. 2 Influence of immersion temperature on crater

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# UNDERVEHICLE CORROSION TESTING OF ZINC & ZINC ALLOY COATED STEELS

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# UNDERVEHICLE CORROSION TESTING OF ZINC & ZINC ALLOY COATED STEELS

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## ABSTRACT

Undervehicle and on-vehicle coupon corrosion test programs were initiated by Dofasco Inc. in 1981, using two commercial trucks operated in the deicing salt/snow belt area of Southern Ontario, Canada.

The purpose was to investigate the relative corrosion performance of numerous zinc and zinc alloy coated steels.

Seventeen coated steels were tested.

Results to date indicate that the hot dip coated steels with the thicker coatings are outperforming the electrolytic coated steels in both the unpainted and phosphated/ cathodic primed conditions. Fully painted on-vehicle test coupons show minimal corrosion and little difference to date.

## INTRODUCTION

IN THE LAST FEW YEARS, there has been an explosion of new coated steel products for automotive applications, mainly from electrogalvanizing lines. Corrosion resistance claims for most of these new electrodeposited zinc alloy coated steels, based on salt spray testing, have ranged from two to ten times the corrosion resistance of an equivalent thickness of zinc (1-9)*. This implies that these new coated steels with low coating weights can be substituted for conventional hot dip zinc coated steels and offer similar corrosion resistance.

This investigation is focused on a direct comparison of the corrosion resistance of the new electrolytic zinc and zinc alloy coated steels with the conventional hot dip coated steels of higher coating weight using coupons mounted on vehicles operated in the deicing salt/snow belt area of Southern Ontario, Canada. This location is considered a severe corrosive environment for vehicles by the automotive industry (10).

Our test program began in December, 1981, using two transport trucks. It consists of both undervehicle and on-vehicle exposure of 17 coated materials in each of three conditions:

(a) Unpainted.
(b) Zinc phosphated and cathodic ELPO primed.
(c) Full automotive paint system.

The test materials were obtained from various suppliers and are listed in Table 1. All were commercially produced except for item numbers 14 and 15 which were produced on a pilot line. Three of the coated materials joined the program one year after the start. These are materials with item numbers 4, 10, and 16, as shown in Table 1.

The two trucks were each fitted with one 2.15 metre long undervehicle test rack, and one 2.15 metre long front bumper (on-vehicle) rack (Figures 1 and 2).

A total of 492 coupons were installed:

- 232 coupons were installed in the unpainted condition and all have been removed and evaluated (one and two year exposures).

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* Numbers in parentheses designate references at the end of the paper.

- 232 coupons were installed in the phosphated and primed condition and approximately one-half of these have been removed and evaluated (three and four year exposures).

- 28 coupons were installed in the fully painted condition on the front bumpers and all are still under test, having been exposed since December, 1981.

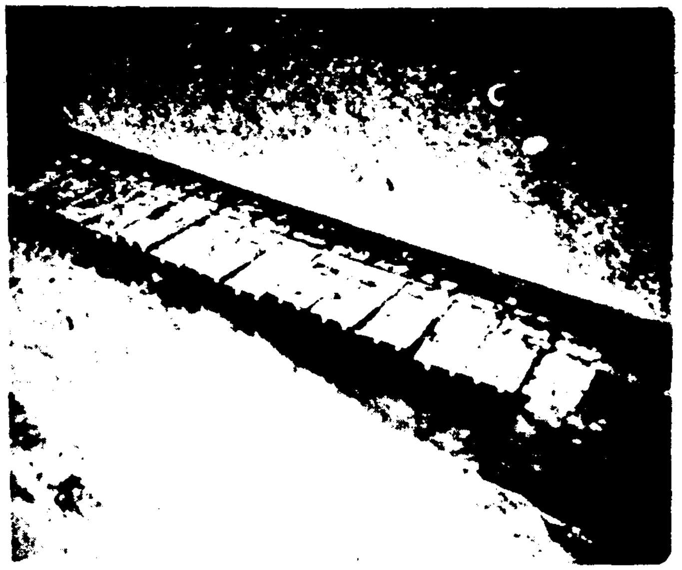

FIGURE 1B - CLOSE-UP OF "UNDER" VEHICLE TEST RACK

TABLE 1 - TEST MATERIALS

| ITEM | MATERIAL TYPE | COATING WT./SIDE* ($g/m^2$) | STEEL THICKNESS (mm) |
|---|---|---|---|
| | HOT DIP | | |
| 1 | Galvanized 1 | 120/150 | 0.71 |
| 2 | Galvanized 2 | 100/120 | 0.90 |
| 3 | Galvanized 3 | 55/90 | 0.45 |
| 4 | Zn/5 Al | 90/120 | 0.63 |
| 5 | Galvannealed 1 | 80/120 | 1.42 |
| 6 | Galvannealed 2 | 75/85 | 0.89 |
| 7 | One Side Galvannealed | 66 | 0.66 |
| 8 | 55 Al/Zn | 75/100 | 0.64 |
| | ZINC RICH PRIMER | | |
| 9 | One Side Zincrometal | 40 | 0.92 |
| | ONE SIDE ELECTRODEPOSITED | | |
| 10 | Electro Zn/15 Ni/0.4 Co | 20 | 0.70 |
| 11 | Electro Zn/15 Ni/0.4 Co | 37 | 0.70 |
| 12 | Electro Zn/16 Ni | 20 | 0.68 |
| 13 | Electro Zn/16 Ni | 40 | 0.68 |
| 14 | Electro Zn/16 Al | 25 | 0.68 |
| 15 | Electro Zn/22 Al | 40 | 0.68 |
| 16 | Electro Zn + $Cr/CrO_x$ | 56 | 0.77 |
| 17 | Electro Zn | 90 | 0.88 |
| | UNCOATED | | |
| 18 | Cold Rolled Steel | 0 | 0.51 |

* The steel industry has traditionally followed the ASTM coating weight designation (e.g. G90, G60). However, most automotive companies are now revising and specifying their coating weight limits in grams per square metre per side.

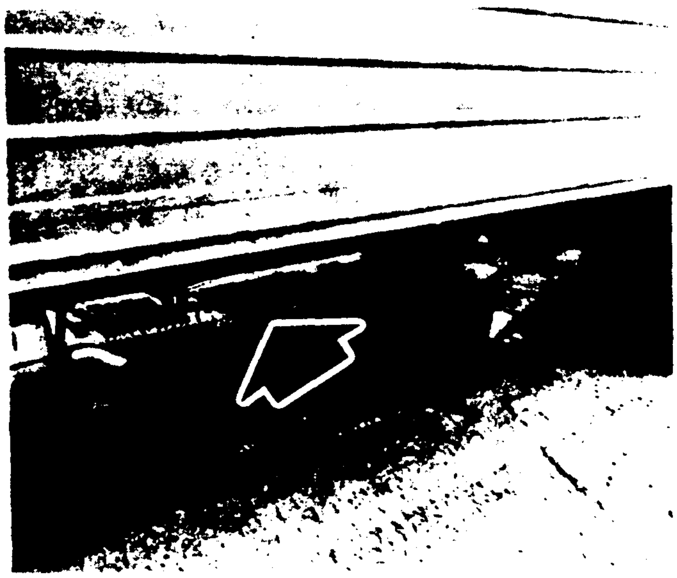

FIGURE 1A - LOCATION OF "UNDER" VEHICLE TEST RACK


FIGURE 2 - "ON" VEHICLE TEST RACK

## TEST METHOD

COUPON PREPARATION

(1) Undervehicle Test: Test coupons 50 mm x 125 mm x thickness of each material were cut from larger sheets, identified and degreased using methyl ethyl ketone. Zincrometal® was not degreased and was tested as produced (unoiled).

Coating weights were measured for each material using weigh-strip-weigh techniques. Each coupon was weighed prior to assembly into the test configurations shown in Figure 3 for one side coated steels, and in Figure 4 for two side coated steels. The coupons were neither formed nor scribed in this test.

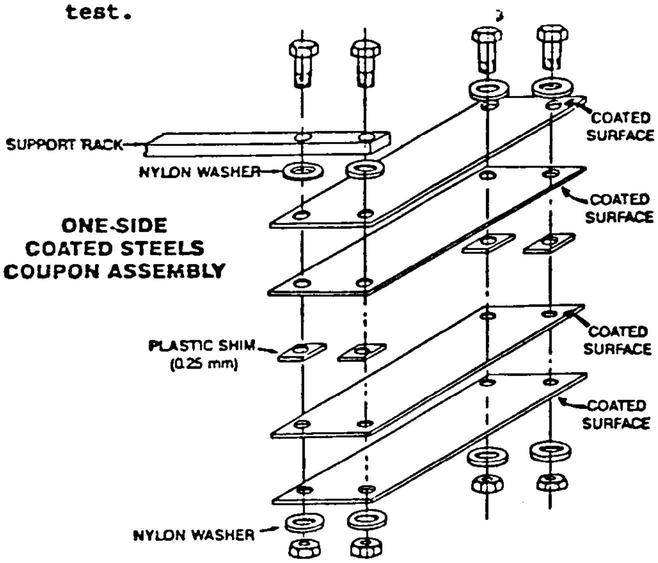


Figure 3
Test assembly, one side coated steels

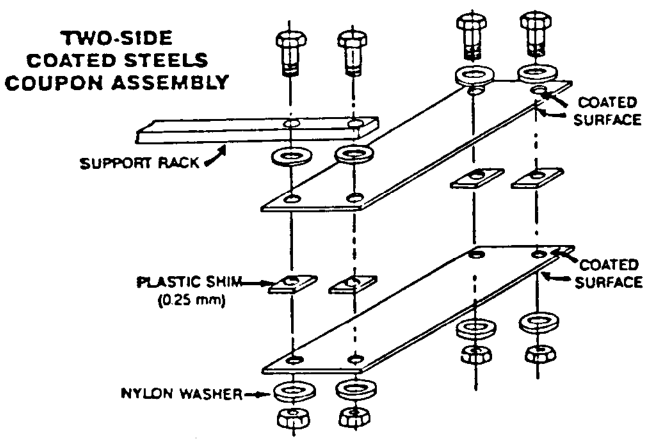


Figure 4
Test assembly, Two side coated steel

The assembly method follows the SAE J1293 "Undervehicle Corrosion Test" Recommended Practice. The only modification was the inclusion of four, rather than two coupons in the test assembly for one side coated steels. This allowed an evaluation of the coated steel in both exposed and crevice conditions.

All the materials in the undervehicle test were tested in two conditions:

(a) unpainted,
(b) zinc phosphated and cathodic ELPO primed.

(2) On-Vehicle Test: Flat panels measuring 75 mm x 150 mm were used for this test which involves exposing duplicate painted and scribed samples on the front bumper of the test vehicles. No unpainted samples were included in this test.

(3) Zinc Phosphate, Cathodic ELPO Primer and Top Coat: The "undervehicle" test assemblies to be ELPO primed, as well as all the "on-vehicle" samples, were laboratory pretreated with EP-1 (aim coating weight 150 - 300 mg/ft$^2$) by Parker Laboratories, Detroit.

The black ELPO paint primer was applied at the GM Technical Centre, Fisher Body Laboratories. Cathodic ELPO ED-3002V (ultra-filtered) was deposited to a dry film thickness of 15 µm at 300 Volts per GM 9984017 specification.

For the undervehicle test, the pretreatment and cathodic primer were applied on the fully assembled coupons to simulate actual production conditions. In general, the ELPO coating penetrated the 0.25 mm crevice, although on occasion, the primer was noted to have less than the required 15 µm thickness.

The ELPO primed "on-vehicle" coupons were sealed and top coated at Dofasco with a white solution acrylic lacquer in accordance with GM test method TM 55-34. A vertical scribe 110 mm long was made in the centre of the panel per GM specification 9102 P.

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## EXPOSURE PERIOD

Two transport trucks were used in this test program. The test coupons have been exposed for up to four winters (1225 days), with evaluations after one, two, three, and four winters. Both trucks were driven in the snow belt region of Southern Ontario where deicing salts are used extensively.

## EVALUATION PROCEDURE

The detailed evaluation procedure is described fully in SAE Recommended Practice J1293, "Undervehicle Corrosion Test" (11).

Briefly, the test assemblies were removed from the vehicle test rack, disassembled and the individual coupons washed in warm water using a non-metallic scrub brush.

(1) Unpainted Materials: Three different criteria were used to evaluate the corrosion performance of the test materials in the unpainted condition. The evaluation for each test material included two exposed surfaces and two crevice surfaces for each nested assembly on each truck:

(a) Uniform Thickness Loss (Micrometres): This was determined by first removing all corrosion products according to ASTM G1-81, then determining the weight loss of each coupon in the assembly, and finally calculating coating thickness loss assuming a nominal exposed area of 50 mm x 125 mm x two surfaces and appropriate coating density.

This criterion was applicable only to the two side metallic coated steels and was used only if no steel substrate attack had occurred.

(b) Percent Surface Area Showing Base Metal Attack (%): This was determined by measuring the extent of attack on the steel substrate after stripping the remaining metallic coating according to ASTM A90-81. A low power (12x) binocular microscope and a clear plastic grid were used to estimate the percent surface area showing base metal attack. Evidence of steel surface roughening indicated base metal attack.

The corrosion evaluation was restricted to the surface area between the bolt holes at either end of the coupon - an area measuring 50 mm x 80 mm.

(c) Pitting Attack (Micrometres): Again, the corrosion evaluation was restricted to the surface area between the bolt holes.

Pitting was determined by locating the five deepest pits on each steel surface (after stripping the metallic coating) using a low power (12x) binocular microscope, and then measuring pit depth at 200x using a portable depth measuring microscope. The depth of each pit was determined by focusing first on the upper edge of the pit, then on the bottom, with the distance of travel measured on a vernier being the pit depth.

The five deepest pits were measured and an average pit depth calculated for each surface. Results are reported for exposed surfaces, crevice surfaces and the average pit depth for all four surfaces of the material in the test assembly.

(2) ELPO Primed Materials: Prior to evaluating the organic coated steels, the electrodeposited ELPO primer was removed by immersion for approximately one minute in a 1:1 mixture of tetrahydrofuran and dimethylformamide at 60°C (appropriate safety precautions are required when handling these two strong solvents). The metallic coatings were then removed with inhibited hydrochloric acid while Zincrometal was removed with methyl ethyl ketone.

Only two criteria, (b) and (c), were used for evaluating the corrosion performance of the ELPO primed materials.

(3) Fully Painted Materials: The "on" vehicle test coupons were evaluated after washing the painted and scribed surfaces with a mild soap and water solution. Paint creepback from the scribe was then measured. The criterion for failure has been set at $\geq$3 mm either side of the scribe.

## RESULTS AND DISCUSSION

### UNPAINTED MATERIALS

(1) Uniform Thickness Loss: This criterion of evaluation failed to provide meaningful results, and therefore, no results are reported.

The technique was limited to the two side metal coated steels which did not show steel substrate corrosion attack after exposure. The few results obtained were variable. Overall, the corrosion attack was seen as non-uniform, rather than uniform.

(2) Percent Surface Area Showing Base Metal Attack: Table 2 gives the results of percent surface area showing base metal attack of unpainted samples removed after one winter's exposure. The results are given separately for each truck, as each is considered an individual test.

We have grouped the materials in the categories of hot dip, zinc rich primer, electrodeposited and uncoated, and this grouping is consistent for all the tables in the paper.

The one winter exposure results generally indicate the hot dip coatings are still providing either complete corrosion protection to the steel substrate or are just beginning to show steel substrate attack. The electrodeposited coated steels, on the other hand, generally show a substantial area of attack of the steel substrate.

The results of coupons removed after two winters' exposure are shown in Table 3. The results show the same trend as the one winter exposure results and generally show more corrosion has occurred on each of the materials.

The electrodeposited coatings after two winters' exposure are near complete failure in the unpainted condition.

The results shown in Tables 2 and 3 indicate that the hot dip coated coupons out-performed the generally lighter coating weight electrodeposited coated coupons, particularly in the exposed condition.

(3) Pitting Attack: Tables 4 and 5 show the pitting results of the 18 materials (17 coated steels and 1 bare cold rolled steel for reference) after undervehicle exposures of one and two winters in the unpainted condition. Here, too, there are indications that the hot dip coated coupons experienced less pitting than the coupons with the electrodeposited coatings. Once again, the exposed surfaces show this trend more clearly than the crevice surfaces.

In summary, the results of both surface area of attack and pitting obtained on unpainted materials exposed for one and two winters undervehicles, do not substantiate the claims of superior corrosion resistance (based on salt spray) for electrodeposited zinc alloy coatings.

### ZINC PHOSPHATED AND CATHODIC ELPO PRIMED MATERIALS

The expected improvement in corrosion protection of these steels by phosphating and the application of a cathodic electrodeposited primer was observed in our undervehicle coupon corrosion test.

Consequently, the first removal of phosphated and primed materials was delayed until after three winters' exposure, and only one set of test materials from one truck (#781) was removed.

Table 6 shows the results of percent surface area showing base metal attack, and Table 7 shows the results of the pitting evaluation for this set of materials. Generally, the superior corrosion resistance of the hot dip coated coupons versus the coupons with the electrodeposited coatings in the phosphated and primed condition, as in the unpainted condition, is indicated in these two tables.

This set of coupons also provided the first observation that coatings containing higher levels of aluminum appear to have a compatibility problem with the paint system as evidenced by primer blistering following exposure.

TABLE 2 - UNDERVEHICLE CORROSION OF UNPAINTED COUPONS
AFTER 1 WINTER'S EXPOSURE (1981 - 1982)**

PERCENT SURFACE AREA SHOWING BASE METAL ATTACK

| MATERIAL | COATING WT/SIDE ($g/m^2$) | TRUCK NO. 781 EXPOSED SURFACES | TRUCK NO. 781 CREVICE SURFACES | TRUCK NO. 781 AVERAGE (4 SURFACES) | TRUCK NO. 782 EXPOSED SURFACES | TRUCK NO. 782 CREVICE SURFACES | TRUCK NO. 782 AVERAGE (4 SURFACES) |
|---|---|---|---|---|---|---|---|
| **HOT DIP** | | | | | | | |
| Galvanized 1 | 120/150 | 0.5 | 0.5 | 0.5 | 6.5 | 21.0 | 14.0 |
| *Galvanized 1 | 120/150 | 0 | 0 | 0 | 0.5 | 0 | 0.3 |
| Galvanized 2 | 100/120 | 0 | 0.5 | 0.3 | 0.5 | 18.5 | 9.5 |
| Galvanized 3 | 55/90 | 1.0 | 2.0 | 1.5 | 0 | 0.5 | 0.3 |
| *Zn/5 Al | 90/120 | 0 | 0 | 0 | 0 | 0 | 0 |
| Galvannealed 1 | 80/120 | 0 | 5.5 | 2.8 | 0 | 0 | 0 |
| Galvannealed 2 | 75/85 | 0.5 | 0.5 | 0.5 | 0 | 5.0 | 2.5 |
| One Side Galvannealed | 66 | 12.0 | 1.0 | 6.5 | 72.5 | 10.0 | 41.3 |
| 55 Al/Zn | 75/100 | 0.5 | 5.0 | 2.8 | 0 | 0.5 | 0.3 |
| **ZINC RICH PRIMER** | | | | | | | |
| One Side Zincrometal | 40 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| **ONE SIDE ELECTRODEPOSITED** | | | | | | | |
| *Electro Zn/15 Ni/0.4 Co | 20 | 59.4 | 4.0 | 31.7 | 31.0 | 5.3 | 18.0 |
| Electro Zn/15 Ni/0.4 Co | 37 | 4.0 | 9.0 | 6.5 | 42.0 | 1.0 | 22.0 |
| Electro Zn/16 Ni | 20 | 80.0 | 32.0 | 56.0 | 55.0 | 44.0 | 50.0 |
| Electro Zn/16 Ni | 40 | 100.0 | 19.0 | 60.0 | 66.0 | 12.0 | 39.0 |
| Electro Zn/16 Al | 25 | 64.0 | 13.0 | 39.0 | 98.0 | 10.0 | 54.0 |
| Electro Zn/22 Al | 40 | 100.0 | 6.0 | 53.0 | 100.0 | 40.0 | 70.0 |
| *Electro Zn + Cr/$CrO_x$ | 56 | 1.3 | 0 | 0.6 | 16.0 | 0.0 | 8.0 |
| Electro Zn | 90 | 100.0 | 80.0 | 90.0 | 93.0 | 16.0 | 55.0 |
| **UNCOATED** | | | | | | | |
| Cold Rolled Steel | 0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

** 1981 - 1982 Exposure, Truck No. 781 - 192 days, 20500 km; Truck No. 782 - 192 days, 19500 km.
* 1982 - 1983 Exposure, Truck No. 781 - 304 days, 14310 km; Truck No. 782 - 304 days, 14500 km.

TABLE 3 - UNDERVEHICLE CORROSION OF UNPAINTED COUPONS
AFTER 2 WINTER'S EXPOSURE (1981 - 1983)**

PERCENT SURFACE AREA SHOWING BASE METAL ATTACK

| MATERIAL | COATING WT/SIDE ($g/m^2$) | TRUCK NO. 781 EXPOSED SURFACES | TRUCK NO. 781 CREVICE SURFACES | TRUCK NO. 781 AVERAGE (4 SURFACES) | TRUCK NO. 782 EXPOSED SURFACES | TRUCK NO. 782 CREVICE SURFACES | TRUCK NO. 782 AVERAGE (4 SURFACES) |
|---|---|---|---|---|---|---|---|
| **HOT DIP** | | | | | | | |
| Galvanized 1 | 120/150 | 0.8 | 0.3 | 0.6 | 13.0 | 15.0 | 14.0 |
| *Galvanized 1 | 120/150 | 8.5 | 0 | 4.2 | 0 | 0 | 0 |
| Galvanized 2 | 100/120 | 0 | 0.7 | 0.3 | 0.5 | 54.0 | 27.3 |
| Galvanized 3 | 55/90 | 0 | 1.0 | 0.5 | 0 | 10.0 | 5.0 |
| *Zn/5 Al | 90/120 | 1.5 | 1.5 | 1.5 | 0 | 0 | 0 |
| Galvannealed 1 | 80/120 | 0 | 0 | 0 | 1.0 | 1.0 | 1.0 |
| Galvannealed 2 | 75/85 | 0.5 | 0 | 0.3 | 10.5 | 55.0 | 32.8 |
| One Side Galvannealed | 66 | 48.2 | 1.9 | 25.0 | 100.0 | 13.0 | 56.5 |
| 55 Al/Zn | 75/100 | 0.5 | 0 | 0.3 | 15.5 | 8.5 | 12.0 |
| **ZINC RICH PRIMER** | | | | | | | |
| One Side Zincrometal | 40 | 10.5 | 11.0 | 10.8 | 21.5 | 13.0 | 17.3 |
| **ONE SIDE ELECTRODEPOSITED** | | | | | | | |
| *Electro Zn/15 Ni/0.4 Co | 20 | 100.0 | 77.0 | 88.5 | 59.5 | 14.0 | 36.8 |
| Electro Zn/15 Ni/0.4 Co | 37 | 69.0 | 23.0 | 46.0 | 100.0 | 35.0 | 67.5 |
| Electro Zn/16 Ni | 20 | 100.0 | 69.0 | 85.0 | 100.0 | 87.0 | 93.5 |
| Electro Zn/16 Ni | 40 | 70.5 | 5.5 | 38.0 | 100.0 | 58.5 | 79.3 |
| Electro Zn/16 Al | 25 | 100.0 | 17.5 | 59.0 | 100.0 | 68.5 | 84.3 |
| Electro Zn/22 Al | 40 | 99.0 | 9.5 | 54.0 | 100.0 | 53.0 | 76.5 |
| *Electro Zn + Cr/$CrO_x$ | 56 | 100.0 | 19.0 | 59.5 | 100.0 | 8.0 | 54.0 |
| Electro Zn | 90 | 97.0 | 25.0 | 61.0 | 100.0 | 72.0 | 86.0 |
| **UNCOATED** | | | | | | | |
| Cold Rolled Steel | 0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

** 1981 - 1983 Exposure, Truck No. 781 - 660 days, 51000 km; Truck No. 782 - 660 days, 53500 km.
* 1982 - 1984 Exposure, Truck No. 781 - 603 days, 32580 km; Truck No. 782 - 603 days, 44900 km.

TABLE 4 - UNDERVEHICLE CORROSION OF UNPAINTED COUPONS AFTER 1 WINTER'S EXPOSURE (1981 - 1982)**

PITTING ATTACK (MICROMETRES)

| MATERIAL | COATING WT/SIDE ($g/m^2$) | TRUCK NO. 781 | | | TRUCK NO. 782 | | |
|---|---|---|---|---|---|---|---|
| | | EXPOSED SURFACES | CREVICE SURFACES | AVERAGE (4 SURFACES) | EXPOSED SURFACES | CREVICE SURFACES | AVERAGE (4 SURFACES) |
| HOT DIP | | | | | | | |
| Galvanized 1 | 120/150 | 0 | 0 | 0 | 11 | 61 | 36 |
| *Galvanized 1 | 120/150 | 0 | 0 | 0 | 0 | 0 | 0 |
| Galvanized 2 | 100/120 | 0 | 27 | 13 | 4 | 29 | 17 |
| Galvanized 3 | 55/90 | 0 | 0 | 0 | 0 | 11 | 6 |
| *Zn/5 Al | 90/120 | 0 | 0 | 0 | 0 | 0 | 0 |
| Galvannealed 1 | 80/120 | 0 | 66 | 33 | 0 | 7 | 4 |
| Galvannealed 2 | 75/85 | 0 | 22 | 11 | 20 | 9 | 15 |
| One Side Galvannealed | 66 | 37 | 20 | 29 | 67 | 51 | 59 |
| 55 Al/Zn | 75/100 | 37 | 55 | 46 | 7 | 25 | 16 |
| ZINC RICH PRIMER | | | | | | | |
| One Side Zincrometal | 40 | 14 | 14 | 14 | 47 | 71 | 59 |
| ONE SIDE ELECTRODEPOSITED | | | | | | | |
| *Electro Zn/15 Ni/0.4 Co | 20 | 53 | 32 | 42 | 53 | 22 | 38 |
| Electro Zn/15 Ni/0.4 Co | 37 | 31 | 36 | 33 | 40 | 26 | 33 |
| Electro Zn/16 Ni | 20 | 53 | 68 | 61 | 61 | 64 | 63 |
| Electro Zn/16 Ni | 40 | 49 | 51 | 50 | 64 | 57 | 61 |
| Electro Zn/16 Al | 25 | 43 | 43 | 43 | 51 | 49 | 50 |
| Electro Zn/22 Al | 40 | 41 | 38 | 40 | 53 | 50 | 52 |
| *Electro Zn + $Cr/CrO_x$ | 56 | 22 | 0 | 11 | 52 | 0 | 26 |
| Electro Zn | 90 | 46 | 72 | 59 | 49 | 33 | 41 |
| UNCOATED | | | | | | | |
| Cold Rolled Steel | 0 | 87 | 189 | 138 | 91 | 110 | 101 |

** 1981 - 1982 Exposure, Truck No. 781 - 192 days, 20500 km; Truck No. 782 192 days, 19500 km.
* 1982 - 1983 Exposure, Truck No. 781 - 304 days, 14310 km; Truck No. 782 304 days, 14500 km.

TABLE 5 - UNDERVEHICLE CORROSION OF UNPAINTED COUPONS AFTER 2 WINTER'S EXPOSURE (1981 - 1983)**

PITTING ATTACK (MICROMETRES)

| MATERIAL | COATING WT/SIDE ($g/m^2$) | TRUCK NO. 781 | | | TRUCK NO. 782 | | |
|---|---|---|---|---|---|---|---|
| | | EXPOSED SURFACES | CREVICE SURFACES | AVERAGE (4 SURFACES) | EXPOSED SURFACES | CREVICE SURFACES | AVERAGE (4 SURFACES) |
| HOT DIP | | | | | | | |
| Galvanized 1 | 120/150 | 0 | 0 | 0 | 9 | 21 | 15 |
| *Galvanized 1 | 120/150 | 27 | 0 | 14 | 0 | 0 | 0 |
| Galvanized 2 | 100/120 | 0 | 21 | 11 | 0 | 111 | 56 |
| Galvanized 3 | 55/90 | 0 | 0 | 0 | 0 | 30 | 15 |
| *Zn/5 Al | 90/120 | 25 | 0 | 13 | 0 | 0 | 0 |
| Galvannealed 1 | 80/120 | 0 | 0 | 0 | 12 | 32 | 22 |
| Galvannealed 2 | 75/85 | 21 | 0 | 11 | 45 | 128 | 86 |
| One Side Galvannealed | 66 | 58 | 37 | 48 | 77 | 56 | 67 |
| 55 Al/Zn | 75/100 | 0 | 0 | 0 | 39 | 58 | 48 |
| ZINC RICH PRIMER | | | | | | | |
| One Side Zincrometal | 40 | 28 | 79 | 53 | 76 | 70 | 73 |
| ONE SIDE ELECTRODEPOSITED | | | | | | | |
| *Electro Zn/15 Ni/0.4 Co | 20 | 154 | 170 | 162 | 95 | 95 | 95 |
| Electro Zn/15 Ni/0.4 Co | 37 | 72 | 77 | 75 | 81 | 81 | 81 |
| Electro Zn/16 Ni | 20 | 77 | 90 | 83 | 92 | 107 | 100 |
| Electro Zn/16 Ni | 40 | 79 | 67 | 73 | 114 | 141 | 128 |
| Electro Zn/16 Al | 25 | 77 | 51 | 64 | 117 | 77 | 97 |
| Electro Zn/22 Al | 40 | 72 | 57 | 64 | 86 | 94 | 90 |
| *Electro Zn + $Cr/CrO_x$ | 56 | 115 | 112 | 114 | 138 | 96 | 117 |
| Electro Zn | 90 | 64 | 64 | 64 | 105 | 134 | 120 |
| UNCOATED | | | | | | | |
| Cold Rolled Steel | 0 | >250 | >250 | >250 | >250 | >250 | >250 |

** 1981 - 1983 Exposure, Truck No. 781 - 660 days, 51000 km; Truck No. 782 - 660 days, 53500 km.
* 1982 - 1984 Exposure, Truck No. 781 - 603 days, 32580 km; Truck No. 782 - 603 days, 44900 km.

TABLE 6 - UNDERVEHICLE CORROSION OF ZINC PHOSPHATED AND ELPO PRIMED COUPONS AFTER 3 WINTER'S EXPOSURE (1981 - 1984)**

PERCENT SURFACE AREA SHOWING BASE METAL ATTACK

| MATERIAL | COATING WT/SIDE ($g/m^2$) | TRUCK NO. 781 | | |
|---|---|---|---|---|
| | | ONE EXPOSED[1] SURFACE | TWO CREVICE SURFACES | AVERAGE (3 SURFACES) |
| HOT DIP | | | | |
| Galvanized 1 | 120/150 | 1.0 | 1.0 | 1.0 |
| *Galvanized 1 | 120/150 | 0 | 0 | 0 |
| Galvanized 2 | 100/120 | 0 | 0 | 0 |
| Galvanized 3 | 55/90 | 1.0 | 1.0 | 1.0 |
| *Zn /5 Al | 90/120 | 0 | 0 | 0 |
| Galvannealed 1 | 80/120 | 0 | 0 | 0 |
| Galvannealed 2 | 75/85 | 0 | 0 | 0 |
| One Side Galvannealed | 66 | 1.0 | 0 | 0.3 |
| 55 Al/Zn | 75/100 | 33.0 | 21.0 | 25.0 |
| ZINC RICH PRIMER | | | | |
| One Side Zincrometal | 40 | 1.0 | 0 | 0.3 |
| ONE SIDE ELECTRODEPOSITED | | | | |
| *Electro Zn/15 Ni/0.4 Co | 20 | 3.0 | 12.0 | 9.0 |
| Electro Zn/15 Ni/0.4 Co | 37 | 90.0 | 33.0 | 52.0 |
| Electro Zn/16 Ni | 20 | 54.0 | 10.5 | 25.0 |
| Electro Zn/16 Ni | 40 | 9.0 | 7.0 | 8.0 |
| Electro Zn/16 Al | 25 | 36.0 | 23.5 | 27.7 |
| Electro Zn/22 Al | 40 | 20.0 | 15.0 | 16.7 |
| *Electro Zn + $Cr/CrO_x$ | 56 | 2.0 | 4.5 | 3.7 |
| Electro Zn | 90 | 13.0 | 13.0 | 13.0 |
| UNCOATED | | | | |
| Cold Rolled Steel | 0 | 1.0 | 20.0 | 13.7 |

** 1981 - 1984 Exposure, 959 days, 71000 km.
* 1982 - 1985 Exposure, 1195 days, 67067 km.
[1] Top surface was accidentally shot blasted During repainting of truck. Results shown refer to bottom exposed surface only.

TABLE 7 - UNDERVEHICLE CORROSION OF ZINC PHOSPHATED AND ELPO PRIMED COUPONS AFTER 3 WINTER'S EXPOSURE (1981 - 1984)**

PITTING ATTACK (MICROMETRES)

| MATERIAL | COATING WT/SIDE ($g/m^2$) | TRUCK NO. 781 | | |
|---|---|---|---|---|
| | | ONE EXPOSED[1] SURFACE | TWO CREVICE SURFACES | AVERAGE (3 SURFACES) |
| HOT DIP | | | | |
| Galvanized 1 | 120/150 | 0 | 0 | 0 |
| *Galvanized 1 | 120/150 | 0 | 0 | 0 |
| Galvanized 2 | 100/120 | 0 | 0 | 0 |
| Galvanized 3 | 55/90 | 22*** | 30**** | 27 |
| *Zn/5 Al | 90/120 | 0 | 0 | 0 |
| Galvannealed 1 | 80/120 | 0 | 0 | 0 |
| Galvannealed 2 | 75/85 | 0 | 0 | 0 |
| One Side Galvannealed | 66 | 39 | 0 | 13 |
| 55 Al/Zn | 75/100 | 103 | 72 | 82 |
| ZINC RICH PRIMER | | | | |
| One Side Zincrometal | 40 | 0 | 0 | 0 |
| ONE SIDE ELECTRODEPOSITED | | | | |
| *Electro Zn/15 Ni/0.4 Co | 20 | 73 | 57 | 62 |
| Electro Zn/15 Ni/0.4 Co | 37 | 33 | 79 | 63 |
| Electro Zn/16 Ni | 20 | 128 | 149 | 142 |
| Electro Zn/16 Ni | 40 | 69 | 37 | 47 |
| Electro Zn/16 Al | 25 | 130 | 176 | 160 |
| Electro Zn/22 Al | 40 | 122 | 97 | 105 |
| *Electro Zn + $Cr/CrO_x$ | 56 | 53 | 39 | 43 |
| Electro Zn | 90 | 124 | 57 | 79 |
| UNCOATED | | | | |
| Cold Rolled Steel | 0 | 57 | 189 | 145 |

** 1981 - 1984 Exposure, 959 days, 71000 km.
* 1982 - 1985 Exposure, 1195 days, 67067 km.
*** All pitting limited to a 4 $mm^2$ area.
**** All pitting limited to a 7 $mm^2$ area.
[1] Top surface was accidentally shot blasted during repainting of truck. Results shown refer to bottom exposed surface only.

The following year, another set of phosphated and primed test materials were removed from the other truck (#782). These materials were exposed for four winters and the results are shown in Tables 8 and 9. Again, the results agreed with the findings from earlier removals. Two additional sets of materials remain for future removals.

Most of the three year and four year test coupons exhibited some blistering of the cathodic primer predominantly on the exposed surfaces. The degree of "cratering" of the cured primed surface was evaluated quantitatively before exposure, but no relationship was found between cratering and blistering after exposure.

Some materials that exhibited a dense cratered surface (eg. Zincrometal ), were not blistered after exposure, and some materials that showed little or no cratering (e.g. 55 Al/Zn) were blistered after exposure.

FULL AUTOMOTIVE PAINTED MATERIALS

All the fully painted test materials exposed on the front bumper for four years (December 5, 1981 to April 13, 1985) are peforming well with no discernible scribe creep. The samples were reinstalled for additional exposure.

## FUTURE WORK

A new vehicle test program was initiated in November, 1984, and involves the detailed "on" and "under" vehicle testing of equivalent coating thicknesses (100 $g/m^2$ per side) of electrozinc and hot dip galvanized. Hot dip galvannealed (60 $g/m^2$ per side) is also included in this study.

Coupons in both the unpainted and in the phosphated and primed (EP-3/Uniprime 3150A) condition are on test.

## CONCLUSIONS

Because of the large number of test materials examined and the limited amount of testing space available on a truck, it was not possible to incorporate enough samples to determine statistically significant conclusions. However, there are indications from the test coupons examined that:

(1) The hot dip coated steels are generally outperforming the lighter electrodeposited coated steels in the unpainted condition.

(2) Compared to the unpainted materials, the pretreated and cathodically ELPO primed test materials show improvement in corrosion performance. However, once again, the hot dip coated steels were generally observed to have less corrosion than the electrodeposited coated steels.

**TABLE 8 - UNDERVEHICLE CORROSION OF ZINC PHOSPHATED AND ELPO PRIMED COUPONS AFTER 4 WINTER'S EXPOSURE (1981 - 1985)****

**PERCENT SURFACE AREA SHOWING BASE METAL ATTACK**

| MATERIAL | COATING WT/SIDE ($g/m^2$) | TRUCK NO. 782 EXPOSED SURFACES | TRUCK NO. 782 CREVICE SURFACES | TRUCK NO. 782 AVERAGE (4 SURFACES) |
|---|---|---|---|---|
| **HOT DIP** | | | | |
| Galvanized 1 | 120/150 | 0 | 0 | 0 |
| *Galvanized 1 | 120/150 | -- | -- | -- |
| Galvanized 2 | 100/120 | 0 | 0 | 0 |
| Galvanized 3 | 55/90 | 0.5 | 0 | 0.3 |
| *Zn/5 Al | 90/120 | -- | -- | -- |
| Galvannealed 1 | 80/120 | 0 | 0 | 0 |
| Galvannealed 2 | 75/85 | 0.5 | 0.5 | 0.5 |
| One Side Galvannealed | 66 | 7.5 | 1.0 | 4.3 |
| 55 Al/Zn | 75/100 | 37.5 | 7.8 | 22.7 |
| **ZINC RICH PRIMER** | | | | |
| One Side Zincrometal | 40 | 0 | 0 | 0 |
| **ONE SIDE ELECTRODEPOSITED** | | | | |
| *Electro Zn/15 Ni/0.4 Co | 20 | -- | -- | -- |
| Electro Zn/15 Ni/0.4 Co | 37 | 40.0 | 15.0 | 27.5 |
| Electro Zn/16 Ni | 20 | 53.8 | 7.5 | 30.6 |
| Electro Zn/16 Ni | 40 | 9.4 | 8.8 | 9.1 |
| Electro Zn/16 Al | 25 | 48.8 | 25.6 | 37.2 |
| Electro Zn/22 Al | 40 | 71.3 | 25.9 | 48.6 |
| *Electro Zn + $Cr/CrO_x$ | 56 | -- | -- | -- |
| Electro Zn | 90 | 8.4 | 5.0 | 6.7 |
| **UNCOATED** | | | | |
| Cold Rolled Steel | 0 | 3 | 5 | 4 |

** 1981 - 1985 Exposure, 1225 days, 107000 km.
* 1982 - 1986 Exposure, data available in 1986.

**TABLE 9 - UNDERVEHICLE CORROSION OF ZINC PHOSPHATED AND ELPO PRIMED COUPONS AFTER 4 WINTER'S EXPOSURE (1981 - 1985)****

**PITTING ATTACK (MICROMETRES)**

| MATERIAL | COATING WT/SIDE ($g/m^2$) | TRUCK NO. 782 EXPOSED SURFACES | TRUCK NO. 782 CREVICE SURFACES | TRUCK NO. 782 AVERAGE (4 SURFACES) |
|---|---|---|---|---|
| **HOT DIP** | | | | |
| Galvanized 1 | 120/150 | 0 | 0 | 0 |
| *Galvanized 1 | 120/150 | -- | -- | -- |
| Galvanized 2 | 100/120 | 0 | 0 | 0 |
| Galvanized 3 | 55/90 | 0 | 0 | 0 |
| *Zn/5 Al | 90/120 | -- | -- | -- |
| Galvannealed 1 | 80/120 | 0 | 0 | 0 |
| Galvannealed 2 | 75/85 | 11 | 13 | 12 |
| One Side Galvannealed | 66 | 102 | 16 | 59 |
| 55 Al/Zn | 75/100 | 90 | 74 | 82 |
| **ZINC RICH PRIMER** | | | | |
| One Side Zincrometal | 40 | 0 | 0 | 0 |
| **ONE SIDE ELECTRODEPOSITED** | | | | |
| *Electro Zn/15 Ni/0.4 Co | 20 | -- | -- | -- |
| Electro Zn/15 Ni/0.4 Co | 37 | 36 | 41 | 38 |
| Electro Zn/16 Ni | 20 | 101 | 61 | 81 |
| Electro Zn/16 Ni | 40 | 74 | 43 | 59 |
| Electro Zn/16 Al | 25 | 117 | 88 | 102 |
| Electro Zn/22 Al | 40 | 142 | 109 | 125 |
| *Electro Zn + $Cr/CrO^x$ | 56 | -- | -- | -- |
| Electro Zn | 90 | 82 | 67 | 75 |
| **UNCOATED** | | | | |
| Cold Rolled Steel | 0 | 73 | 92 | 82 |

** 1981 - 1985 Exposure, 1225 days, 107000 km.
* 1982 - 1986 Exposure, data available in 1986.

## ACKNOWLEDGEMENTS

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(11) Society of Automotive Engineers, Inc., "Undervehicle Corrosion Test"; 1985 SAE Handbook, Vol. 1, Materials; SAE J1293; 1980; 3.37-3.40

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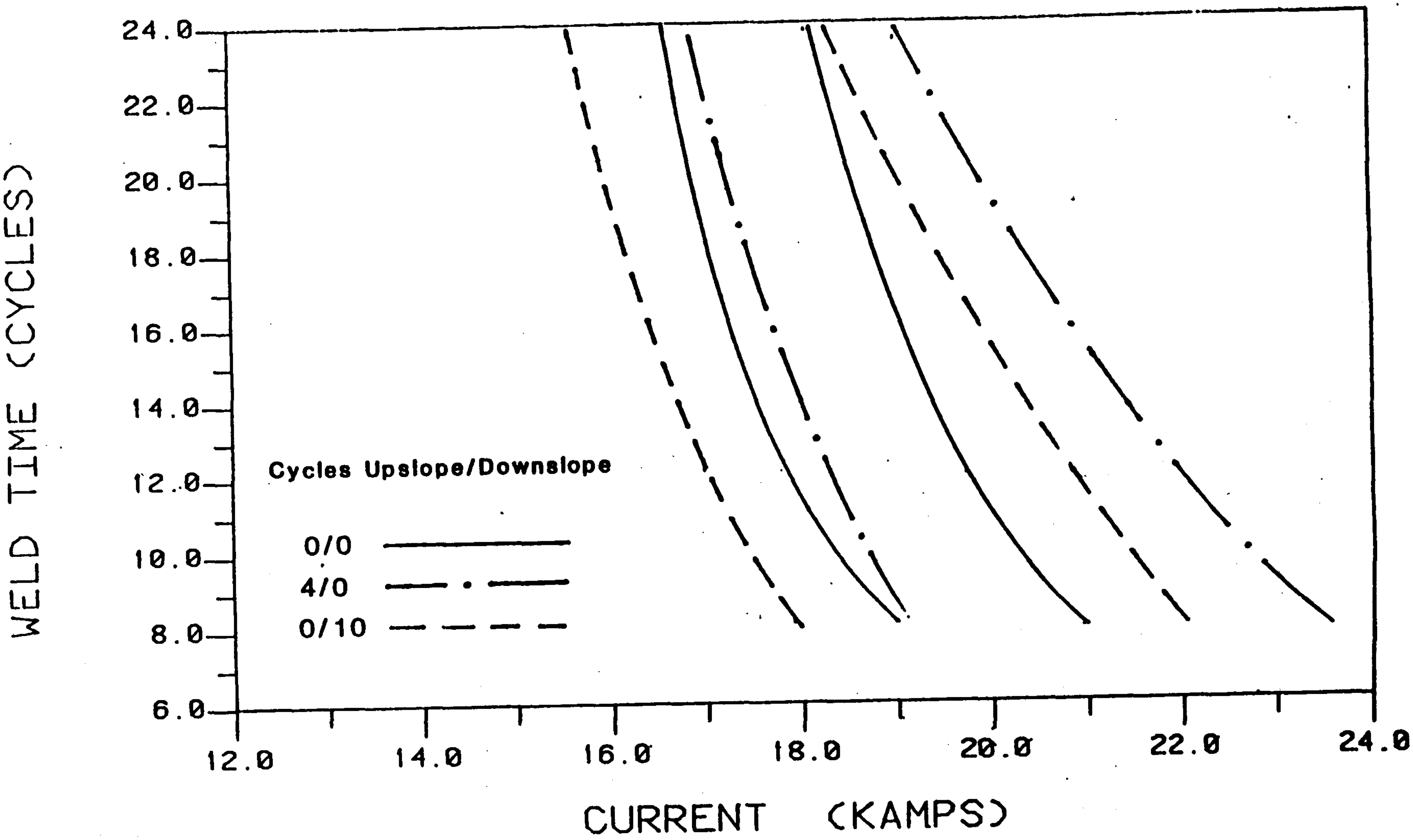


Figure 13 Galfan Lobes with Sloped Current (T.Cone, 1050 lbs.)

**INTERNATIONAL LEAD ZINC RESEARCH ORGANIZATION**

**INTER-OFFICE MEMORANDUM**

**DATE:** November 7, 1985

**TO:** F.E. Goodwin

**FROM:** D.S. Carr

**SUBJECT:** ZM-285 Continuous Galvanizing With GALFAN Alloy - Patent and Trademark Status

The following report of ILZRO patents and trademarks for the GALFAN alloy (Zn-5%Al-mischmetal) and coating process gives the current status as of November 1, 1985.

GALFAN Patents Issued

| Country | Patent Number | Date Issued |
|---|---|---|
| United States | 4,448,748 | May 15, 1984 |
| Argentina | 227,220 | September 30, 1982 |
| Belgium | 882,431<br>887,121 | March 25, 1980<br>January 6, 1981 |
| Canada | 1,175,686 | October 9, 1984 |
| East Germany | 220,342 | March 27, 1985 |
| European (EPC) | 48,270 | August 14, 1985 |
| South Africa | 82/0091 | November 24, 1982 |
| Spain | 508,771 | May 3, 1983 |
| Taiwan | 17, 916 | November 1, 1982 |

GALFAN Trademark Registrations

| | | |
|---|---|---|
| Benelux | 375,388 | August 4, 1981 |
| Bophuthatswana | 84/0177 | March 19, 1984 |
| Finland | 92,853 | June 5, 1985 |
| Frnace | 1,184,193 | October 2, 1981 |
| Norway | 119,540 | March 20, 1985 |
| South Africa | 84/0191 | May 29, 1985 |

| Country | Patent Number | Date Issued |
|---|---|---|
| South West Africa | 84/0168 | March 14, 1984 |
| Sweden | 181,144 | April 23, 1982 |
| Transkei | 84/0183 | May 29, 1985 |
| West Germany | 1,049,001 | May 30, 1983 |

We noted that this information will be presented at the Seventh Galfan Licensees Meeting in Brussels on December 5, 1985.

Dodd S. Carr

Dodd S. Carr
Manager, Chemistry, Electrochemistry
and Patents

cc: J.F. Cole
C.E. Roberts