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Industrial Coatings: Properties, Applications Quality, and Environmental Compliance

Proceedings of the
ASM/ESD Advanced Coatings Technology Conference
2-5 November 1992
Chicago, Illinois, USA

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Published by
ASM International®
Materials Park, Ohio 44073-0002

First printing, November 1992

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Library of Congress Cataloging Card Number: 92-82926
ISBN: 0-87170-461-7
SAN: 204-7586

Production Manager
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ASM International®
Materials Park, OH 44073-0002

Printed in the United States of America

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ENGINEERING PROPERTIES OF COATINGS

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The Development of Intermetallic Phases in Galvannealed Coatings

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ABSTRACT

In galvanizing a coating of zinc is applied to steel for protection from corrosion. In the continuous galvannealing process, the galvanized sheet enters an annealer after leaving the zinc bath. The sheet undergoes a very short time annealing cycle for the purpose of converting the zinc coating to desirable Fe-Zn intermetallics. However it is difficult to determine the exact time-temperature cycle that the sheet undergoes in the annealer. In this study galvanized strips were subjected to very short time anneals in the 500°C range using a Gleeble system. Optical microscopy, scanning electron microscopy and electron microanalysis techniques were used to detect and measure the extent of phases that develop during the annealing process. These observations were compared to results obtained from commercial galvannealed materials, allowing an estimate of the commercial time-temperature cycle.

ON A HOT DIP GALVANIZING LINE, cold rolled strip of known chemistry and process history is continuously heat treated in a reducing atmosphere prior to coating. This treatment provides the steel substrate with the desired mechanical properties and reduces the oxides on the surface of the steel strip, increasing the wettability of the steel by molten zinc (1). The steel strip is then fed into a molten zinc bath maintained at about 450°C. The bath contains up to 0.3 wt% Al to suppress the formation of brittle Fe-Zn intermetallics and reduce the oxidation of the zinc bath (2). As the zinc coated steel strip emerges from the bath, it passes through coating weight control dies which ensure a uniform coating of the desired thickness. Hot dip galvanized sheet consists of an essentially pure zinc coating on a steel substrate.

In the galvannealing process, the strip then travels through a galvannealing furnace which heats the strip to about 500°C for times up to twenty seconds. Galvannealing converts the zinc coated steel to the desired Fe-Zn intermetallics through diffusion controlled reactions. Galvannealed sheets have superior welding properties and corrosion resistance compared to galvanized pure zinc coatings (3). Paint adherence is also better for optimum galvannealed steels (4). Therefore galvannealed sheets are being used for corrosion resistant body panels in automobiles. It is also less expensive to produce this than electroplated Zn-alloy coatings (3).

The Fe-Zn equilibrium diagram shows four intermetallic compounds stable at galvannealing temperatures. The four intermetallics are listed in table 1.

Table I. Fe-Zn Intermetallics (5)

Phase	Formula	Crystal Structure
ζ	$FeZn_{13}$	Monoclinic
δ_1	$FeZn_7$	Hexagonal
Γ_1	$FeZn_4$	FCC
Γ	Fe_3Zn_{10}	BCC

The galvannealing treatment has to be controlled to obtain the desired phases in the coating. The presence and the extent of the phases in the coating control properties like paint adherence, formability and powdering resistance (powdering is the peeling of the coating at the interface). Previous studies have indicated that about 9 to 11 wt % Fe content in the coating is required for good formability (6). The Γ phase which forms at the interface is brittle resulting in poor powdering resistance of the coating (3). The δ_1 phase is generally considered to be the most beneficial phase in the coating.

In this study the change in thicknesses of the different phases in the coating were measured as a function of the annealing time. The phase thicknesses were mainly inferred from measurements of iron and zinc concentrations along the width of the coating. It is expected that the phases are in equilibrium, and therefore phases corresponding to any composition can be deduced from the equilibrium Fe-Zn diagram.

Hot dip galvanized steel strips were subjected to short time anneals using a Gleeble system to simulate the galvannealing process. The extent of phases was measured as a function of the annealing time.

EXPERIMENTAL PROCEDURE

All simulated galvannealing studies were conducted on commercial hot dip galvanized steel characterized by Schurman (7). The chemical composition of the base metal and the galvanic coatings are shown in Table II and Table III respectively. The coating weight was 115 g/m^2.

Table II. Chemical analysis of the base metal (wt%)

C	Mn	Si	Cr	Cu	Co	Ni	V	M
0.01	0.27	0.03	0.02	0.01	0.01	0.01	0.01	0.01
P	S	Ti						
0.009	0.01	<0.01						

Table III. Chemical analysis of galvanic coatings (wt %)

Zn	Pb	Ca	Al	Na	Ba	Ni
99.81	0.08	0.01	0.08	0.01	0.01	<0.01

The simulated annealing was carried out using a Gleeble system which heats the sample, according to a programmed cycle, through electrical resistance heating. The heating rate was 100^{0}C/s and the temperature of simulated galvannealing was 500^{0}C. Holding times were 5, 10, 25, 100, 225, 400 and 1000 seconds. The samples were air quenched from the holding temperature. After annealing, the samples were sectioned and prepared for metallography. Some of the galvannealed samples were electroplated with nickel to preserve their edges. The specimens were studied by optical and scanning electron microscopy. Microanalysis, using an electron probe microanalyzer, was carried out to measure the concentration profile across the coating interface. The phase distributions were measured at each annealing time.

DISCUSSION

Figure 1 shows the concentration profile across the hot dip galvanized coating prior to annealing. The steel-zinc interface shows a high concentration of Al, indicating the presence of an Al-rich inhibiting compound,(2) which prevents growth of intermetallics when the steel is in the zinc bath. Figures 2(a) to 2(g) represent the concentration profile obtained from the simulated galvannealed material annealed at 5, 10, 25, 100, 225, 400 and 1000 seconds, respectively. Only the Γ and the δ_1 phases are present in sufficient thicknesses to enable their measurement. The ζ generally forms as crystals distributed in the δ_1 phase in the outer edges of the coating during galvannealing (8).

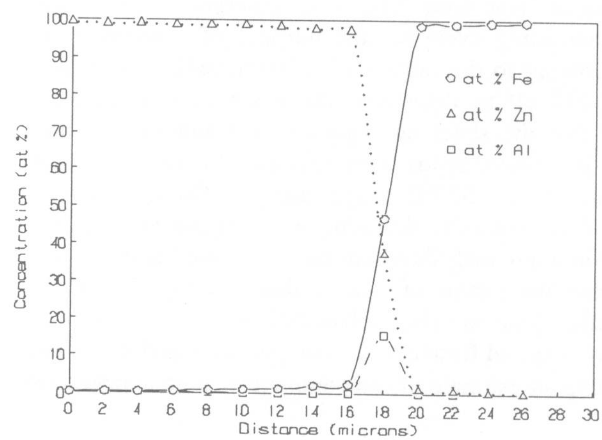


Fig.1: Concentration profile of Fe and Zn in commercial hot dip galvanized coating as a function of distance from the edge of the coating.

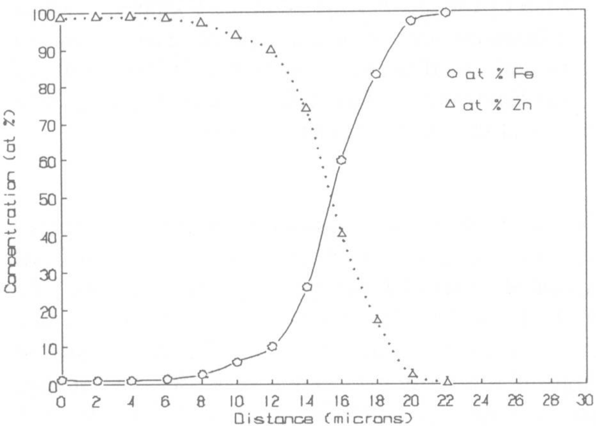


Fig.2(a)

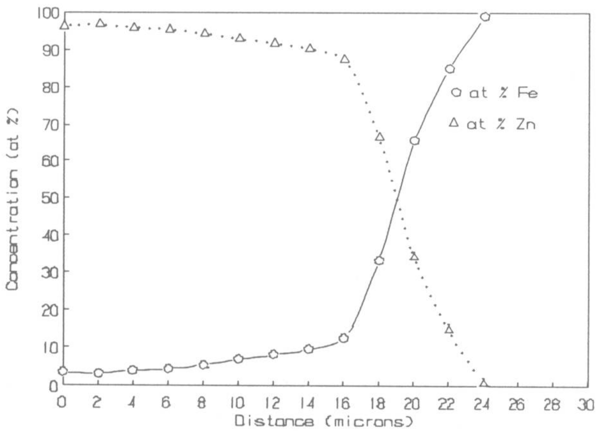
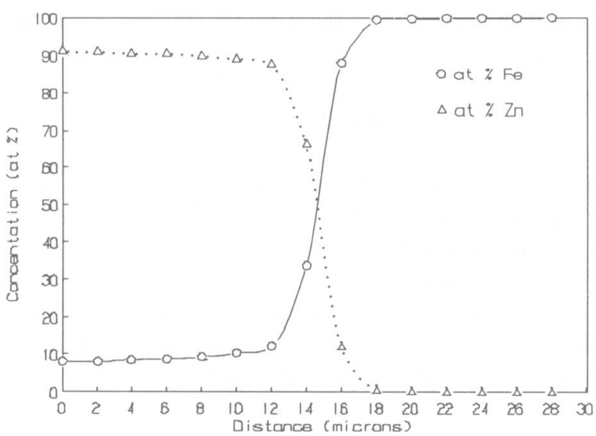


Fig.2(b)



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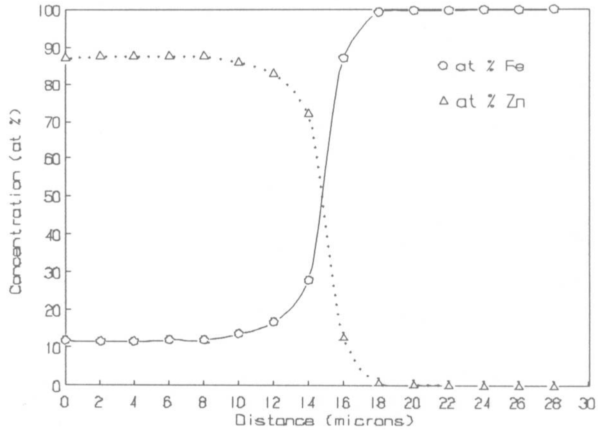

Fig.2(d)

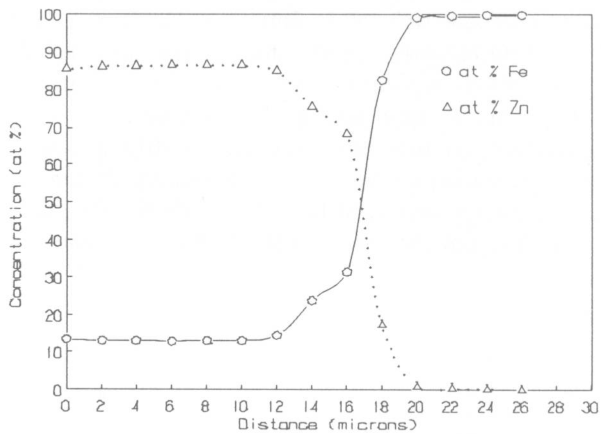

Fig.2(e)

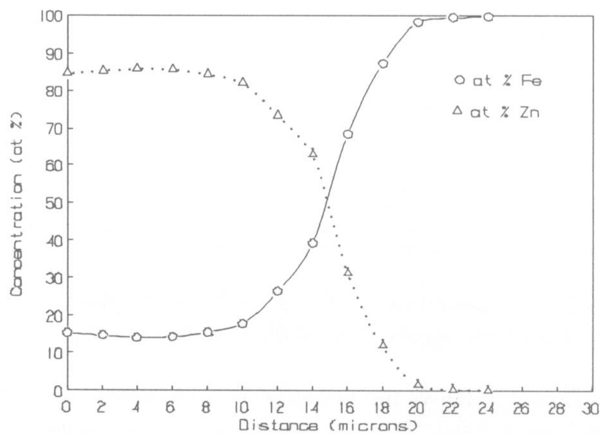

Fig.2(f)

Fig.2: Concentration profile of Fe and Zn in at.wt % as a function of distance from the edge of the coating. Hot dip galvanized steel strips annealed for the following times at 500°C:

a) 5 seconds; b) 10 seconds; c) 25 seconds;
d) 100 seconds; e) 225 seconds; f) 400 seconds;
g) 1000 seconds.

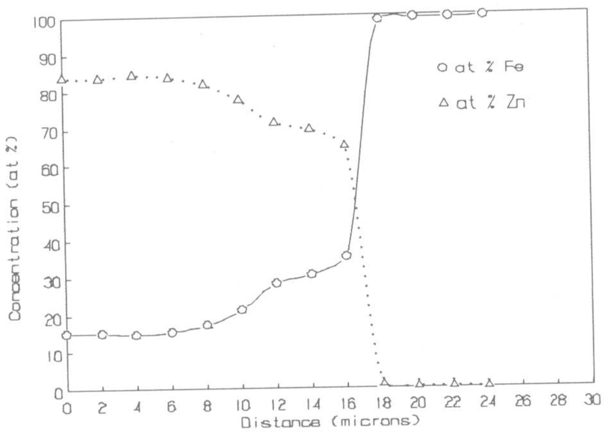

Fig.2(g)

The 5 second annealed sample shows a significant amount of the zinc rich solid solution, η. The iron content in the coating increases rapidly during annealing. The δ_1 phase grows very rapidly to cover most of the coating for annealing times approaching 25 seconds. This is approximately the time that a galvanized strip spends in the annealer during commercial galvannealing. When the annealing time is increased to 100 seconds the thickness of the δ_1 does not increase, but the δ_1 becomes richer in iron.

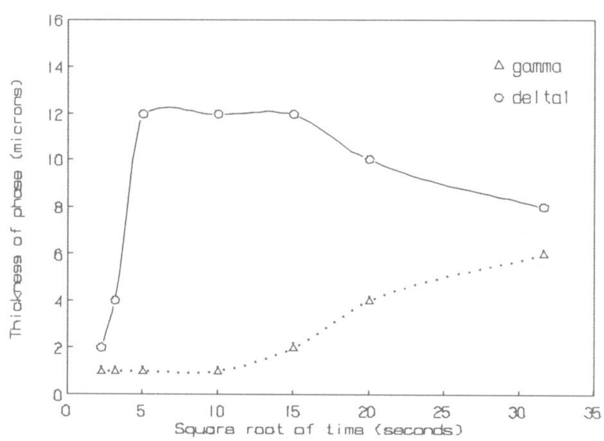

Fig.3: The thickness of the Γ and the δ_1 phase as a function of the square root of the annealing time.

Figure 3 shows the variation in thicknesses of the Γ and δ_1 as a function of the square root of the annealing time. At the annealing time of 225 seconds, it is observed that the δ_1 does not thicken but the Γ phase has begun to grow. Beyond an annealing time of 225 seconds, the Γ phase rapidly grows consuming the δ_1 phase previously formed, as iron content in the coating rises due to interdiffusion of iron and zinc. This is consistent with the observation of Onishi, et al. (9) that the Γ phase nucleates after the formation of both δ_1 and ζ phase. The galvanized steel represents a diffusion couple with a finite quantity of zinc. This limits the growth of the δ_1, and further growth of the Γ is at the expense of the δ_1 phase.

Figure 4 shows the concentration profile obtained across the coating interface for the commercial galvannealed material (coating weight approximately 60 g/m^2). It shows basically only the δ_1 phase with a thin layer of Γ at the iron-zinc interface. The iron content at the edge of the coating is about 12 at %. The coating composition was reported to be about 10.3 % Fe, 0.15 % Al and 0.09 % Pb (10). This would correspond to a simulated galvannealing cycle of about 25 seconds at 500°C.

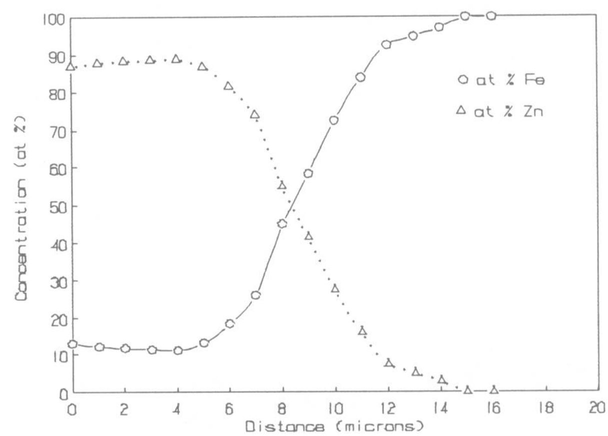

Fig. 4: Concentration profile of Fe and Zn in commercial galvannealed coating as a function of distance from the edge of the coating.

Conclusions

The 25 second simulated galvannealing treatment at 500°C produces a coating structure which appears to correspond closely to that of the commercial galvannealed material. There appears to be an annealing time period between 25 and 225 seconds where the coating essentially remains as the desirable δ_1 phase. Further annealing times result in rapid growth of the undesirable Γ phase.

Acknowledgements

This work is funded by the Rensselaer High Temperature Technology Program, administered by the New York State Energy Research and Development

Authority (NYSERDA). The authors thank Armco, Middletown, OH and Bethlehem Steel, Bethlehem, PA for useful discussions and contributions of material. The authors also thank Mr.Frank Kraft, RPI, for performing the Gleeble simulations.

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Proceedings of the Advanced Coatings Technology Conference, Chicago, Illinois, USA, 3-5 November 1992

Appliances for the Nineties: The Switch to Prepaint

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Abstract

The current and potential uses for prepainted (coil-coated) metal in the Appliance and HVAC (heating/ventilation/air-conditioning) marketplaces are virtually unlimited, and the decision to "go prepaint" is amassing considerable support. The coil coating process is easily able to provide material which meets all of the traditional, and very demanding, performance requirements of the Appliance and HVAC marketplaces. Consequently, it is free to address both the economic and environmental issues head-on, in a way that cannot be matched by traditional spray-applied liquid and powder coatings. Prepainted metal also frees the appliance engineer to let his imagination soar, with regard to innovative designs, joining and fastening techniques, and new end-uses--and allows his/her colleagues in the plant to profitably redirect time and energy previously spend dealing with waste water, EPA emission permits and hazardous waste disposal.

"NOW COMES THE START OF WHAT MAY BE A NEW TREND WITH APPLIANCE MANUFACTURERS: Replacing Powder Coating with prepaint."[1] Taken from a recent issue of *Industrial Finishing*, these are bold words, indeed--but also highly suggestive that the handwriting may be on the wall.

Why Prepaint?

Dr. Marco Wismer, in his keynote address at the 24th Annual Symposium of the Washington Paint Technical Group in 1984, suggested six strategic goals for the coatings industry: corrosion protection, elimination of solvents, conservation of energy, reduction of toxic wastes, cost reductions without sacrificing quality, and improved durability.[2] Since this list represents a continuum, rather than a discreet, explicit list of new mandates for the future, the question naturally arises, "How do I get the most bang for my buck? How can I accomplish as many of these goals as possible, with the highest level of efficiency as possible, as economically--and with as little disruption to my operation--as possible?" The answer? ***PREPAINTED (Coil-coated) METAL.***

It is no secret that more and more far-sighted corporations, headed by visionary leaders, are embracing the coil-coating process each day, and it is no wonder. United Technologies Carrier (City of Industry, California), recently switched their NE/NQ and 48 Series heating/cooling units from spray-applied powder to prepainted metal, and realized an annual savings of $500,000.[3] (This represented 11% of the annual cost to run the plant.)[4] Additional, significant benefits included[5]:

- Elimination of automatic washer
- Elimination of dealing with waste water discharges
- Reduction of hazardous waste by 93 tons/year (50%)
- Reduction of yearly water usage by 3.17 million gallons
- Removal of need for six operating permits for air emissions

Ray Nasuta, Materials Manager for the plant, indicated that "although powder improved product quality somewhat (over liquid, spray-applied coatings), it did not address the issue of waste water sludge disposal inherent in metal-cleaning operations."[6] Nasuta also indicated that "Carrier testing shows that prepainted metal improves corrosion resistance and paint adhesion as compared with (powder) postpaint."[7]

This is an experience being re-created everywhere. At their Knoxville, Tennessee plant, Carrier was able to implement accelerated design strategies as well as significant environmental achievements, through the use of prepainted metal. By replacing outdated batch flow manufacturing with demand flow concepts, orders that once took 8-12 weeks now can be turned around in a matter of days.[8] The facility eliminated eight hazardous waste streams as well as run-off waste water, and thirteen state air permits. Carrier's Plant Manager, Hatcher Meeks, indicated that ". . .the best solution for hazardous waste problems was simple--don't create it."[9] Carrier also has noted that the facility has experienced no need for touch-up operations, and is quite impressed with the durability of prepainted metal. Mr. Meeks has indicated that "the switch to prepaint has resulted in a higher quality product."[10]

Carrier's experience replacing powder was mirrored by competitor Lennox Industries, Inc., which replaced its post-painted urethane with prepainted metal. According to Phillip R. Whitaker, P.E., Corporate Industrial Engineer for Lennox, "Prepainting makes the steel three times more resistant to corrosion than is required by UL Laboratories. Our number one reason for going with prepainted material was its superior corrosion protection. It was also a cost reduction."[11] And so it goes. . . .

What is Prepainted Metal?

. . .And why is it having such a dramatic effect on the way the manufacturers of appliances and HVAC are re-thinking their entire operation, from design through handling characteristics; from environmental considerations through ultimate performance properties; from "just in time delivery" through improvement in bottom line returns?

The use of prepainted metal has become an accepted and practical means of producing a coated part with a quality finish, both in terms of aesthetics and performance. State-of-the-art coil coating lines, sophisticated organic coatings, and a variety of joining and fastening technologies, have provided today's appliance engineer with a cost-effective, totally non-polluting raw material. Manufacturers of refrigerators and freezers have, of course, capitalized on this technology for years, and use coil-coated material as a routine aspect of the manufacturing process.[12] There are, however, many other industries which are discovering both significant savings and substantial performance advantages as they convert to prepainted metal. While this conversion requires careful, well-considered planning, the economic and environmental incentives easily provide the driving force to justify and initiate such a conversion. In the Nineties, a once-neglected consideration--the environment--is presenting a considerable number of concerns to manufacturers, of all types. The coil coating process, which essentially eliminates environmental issues for the end-user, can be a powerful tool for the engineer whose job is to assist his or her company in complying with today's comprehensive regulations. The possibilities for designing with prepainted metal--whether to take advantage of its excellent performance properties, environmental advantages, or adaptability to a wide variety of fastening and joining techniques (including adhesive bonding)--are virtually limitless.

Designing With Premium Organic Coatings

. . .And so, too, is the array of high-quality organic coatings which are available for prepaint applications, using the coil-coating process. The workhorse system used in the appliance industry is one composed of a thermally-crosslinked polyester resin in combination with an amino crosslinking material. The primary advantage of polyesters is the combination of hardness and flexibility which they offer, in addition to their low cost. To the innovative designer, however, other types of prepainted coatings chemistry are readily available, which may be of use in challenging current appliance design concepts. Acrylic resin technology offers superb flow when compared to polyester but with somewhat less flexibility; Dispersion resin coatings, based on polyvinyl chloride (PVC), offer exceptional resistance to aggressive chemicals (acid, bases, etc.); and polyurethane chemistry represents a class of organic coatings with excellent extensibility, which offers the design engineer the means of utilizing prepainted metal where significant drawing properties are required. Epoxy resin technology still dominates the market where primers are needed, and these coatings demonstrate excellent adhesion to the substrate, although they are not as flexible as other resins (e.g., high-molecular weight polyesters and urethanes) which are also being used as primers. Acrylic emulsion technology has come a long way and is gaining acceptance in coil coating applications with its unusual balance of hardness, flexibility, and adhesion properties. While not all of these technologies have equal application in the Appliance and HVAC marketplaces, they nonetheless give some idea of the staggering breadth of potential available to the forward-looking engineer.

Joining and Fastening Techniques

It used to be that the only way to fasten two pieces of prepainted metal was with rivets or screws. While these techniques are still used extensively, other forms of joining allow the engineer to consider new designs which utilize prepainted metal. Some of these new techniques are welding (in the presence of a conductive organic coating), in situ rivetting operations, and adhesive bonding. The latter of this group is generating the most interest since the ability to bond with adhesive offers a tremendous number of options for the design of components utilizing prepainted metal, which can be adhesively bonded to provide a surface undistorted by the fastening process. In addition, adhesively bonded joints are lighter, and have considerably greater surface area than welds or traditional mechanically fastened joints; as a result, stress is distributed over a much greater area. Because of the "sealing" aspect of a bonded joint, it is more resistant to moisture, corrosion resistance is generally improved and noise and vibration may be significantly dampened. "After environmental testing, shear strength is often better than 90% of original strength,"[13] comments George A. Fletcher, Metal Koting-Continuous Colour Cote Limited. In addition to improved strength, the potential for using lighter-gauge metal and increased accommodation of thermal expansion offers today's appliance designers a range of options that is almost limitless. Specific paints and adhesives must, of course, be tested for compatibility with the final design concept, but the overall advantages of adhesive bonding clearly mark it as the wave of the future.

Performance Advantages of Pre-Painted Metal

Easier, More Efficient Handling. The demands of handling and cleaning a smooth strip of metal are considerably less than those of working with preformed parts, which offer limited accessibility for cleaning and pretreating. Coil lines, of course, can operate at very fast line speeds, and advances made by the pretreatment companies now allow for exceptional cleaning and chemical treating of the metal in very short time frames (seconds, in a cleaning or pretreating cell, as opposed to minutes on a spray line). Various chemistries are available to treat the metal, depending on the nature of the final product. The older pretreatments (iron phosphate and zinc phosphate) are still in use today, as well as newer chrome-containing and mixed-metal oxide pretreatments. The most recent advance in pretreatment technology has been the development of dried-in-place pretreatments. These materials are roll-applied, rather than using a spray or immersion system. The main perceived advantage is a significant reduction in pretreatment waste, much of which contains chrome, one of the controlled elements on the hazardous disposal lists. Whatever the method, however, cleaning and pretreating a smooth sheet of metal is done with great efficiency, producing a very uniform surface upon which to paint. It is rare to experience pretreatment build-up or "washer marks" on a coil line, which consequently enhances the performance of the coated metal in moisture sensitivity testing, such as salt spray, humidity cabinet, water immersion, etc.

Greater Uniformity. The coating process used on most coil lines inherently produces uniform coating thickness. Typical dry film thickness variations of no more than ± 0.05 mil are expected, regardless of the line speed. Since a coil line represents a continuous process, it lends itself to dynamic, continuous measurements of certain properties. One such parameter, the dry film thickness (DFT) of the organic coating, can be monitored by use of a beta-backscatter[14] unit. Since most modern coating lines make use of a tandem set-up (i.e., both a primer coater/bake oven and finish coater/bake oven are contained on the same line), end-users have the option to specify a primer, something seldom done on post-paint lines. Given the film thickness control, and the option to select a primer if desired, defect-free films can be produced under tightly-controlled conditions. The cure of the coating on the strip is also very uniform, again due in part to the nature of heating (and curing) a perfectly uniform strip of metal. There are no hot spots in coil ovens, due to substantial airflow through the oven, and no cool spots on the cured strip, as is the case when painting preformed parts, which may have portions of greater mass due to brackets or multiple metal layers which are welded together. These "heat sinks" on preformed metal, which create significant cure differences on the final part, are non-existent with prepainted metal. The uniform application and curing of the organic coating are obvious advantages of the overall performance of the coated metal system, but significant advances in coatings science have contributed equally to the overall performance of the coated, finished part.

Economic Advantages of Prepainted Metal

Nearly 100% Transfer Efficiency. Considering that conventional ***spray losses*** are approximately 65%, and even losses associated with electrostatic spray are ***at least*** 15%, there can be little doubt that coil coating is the most efficient method of painting. The improvement in transfer efficiency over typical spray methods provides a direct savings to the end-user of coil coatings.

100% Usable Material to the End-Customer. Depending on the design and end-use, prepainted material is shipped as completely usable material. Certain notching, slitting, and cut-to-length operations may, of course, reduce this number somewhat. This is not to suggest that defects never occur on the coating line, but the Quality Control operation on a coil line prevents *any* substandard product from reaching the customer.

Direct and Indirect Painting Costs Eliminated. The obvious direct costs associated with operating a post-paint line, such as labor, benefits, equipment repair and energy costs, are eliminated. Some less obvious costs that are often overlooked, however, are costs associated with start-up of ovens, maintenance of booths, ovens, pretreatment tanks, material handling pumps, heating of paint storage vaults, etc.

Hidden Costs Eliminated when Using Prepainted Material. There are myriad costs associated with a post-paint operation that are typically overlooked or--if even considered--are difficult to ascertain. For instance, ***insurance costs*** that are associated with a building storing flammable materials are considerably higher than those for facilities where only forming equipment is housed. Even harder to detail is the cost of floor space. It is estimated that there may be as much as 50% greater utilization of floor space when converting to a prepaint system, and some users who have converted to prepaint from a spray line have experienced 30% in time savings. Certain raw material savings can be experienced, as well, since bare metal does not need to be inventoried, in addition to organic coatings, pretreatment chemicals, *et al.* Perhaps the most insidious--but least tabulated--cost is that required to comply with OSHA and EPA regulations. These ever-increasing burdens start with a few forms, but may well end with the need to employ a department of specialists to handle them. When utilizing prepainted metal, all costs--both direct and indirect--are included in the price of the coated metal, and significant economic advantages are the result.

Environmental Advantages to Using Prepainted Metal

The previous four points briefly discussed some of the economic advantages associated with *not* having to deal with environmental concerns. Most business concerns center, of course, around the economic aspects, but the protection of the environment--both within the workplace and outside the facility itself--involves more than merely the cost of handling each of these concerns. Certainly greater amounts of time and dollars will be needed to handle today's environmental issues, but many issues transcend simply spending money to comply with regulations. Some of the most recent regulations even threaten the user's ability to continue "business as usual." Disposal of hazardous waste is not only becoming increasingly expensive, but also increasingly restrictive. Solid waste landfills are filling-up and are now limiting the extent to which they will accept scrap materials. Hazardous waste landfills are becoming increasingly rare as the long-term maintenance aspects of these landfills become more apparent. Disposal of waste solvents is also becoming more difficult. Only EPA-approved reclaimers can be considered. Gone are the days of using waste solvent for scrap fuel. The EPA, of course, has been given new mandates regarding emissions, and has issued guidelines which are more aggressive than ever. In some cases, the only way to comply may be to shut the doors of some businesses. As more is learned about exposure to solvents in the workplace, greater restrictions will inevitably be placed on the use of certain solvents, and the coatings which contain them.

Dealing with waste, however, seems to be the area of greatest concern. It has been estimated that an automotive line, operating at full capacity, generates seven tons of hazardous waste each 24-hour period. Considering the labor cost to produce the waste, the cost of disposal, the cost of the material which eventually ends in waste, the cost of reporting the waste, and the increased difficulty associated with actually finding a "home" for