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(54) **Title:** HIGH-ALUMINUM ALLOY FOR GENERAL GALVANIZING

(57) **Abstract:** The present invention relates to compositions and processes for the production of high-aluminum alloy. More specifically the patent relates to compositions and processes for the production of high-aluminum alloy for general galvanizing of ferrous materials. In one embodiment, the present invention relates to a unique combination of a zinc-ammonium flux and a molten zinc-aluminum alloy bath containing silicon. The present invention also relates to an improvement in the fluxing step used in the galvanizing process for iron and steel, and high aluminum-content steel made using that improved process.

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HIGH-ALUMINUM ALLOY FOR GENERAL GALVANIZING

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of United States Provisional Patent Application No. 60/804,348, filed June 9, 2006, entitled "High-Aluminum Alloy For General Galvanizing", and United States Provisional Patent Application No. 60/804,358, filed June 9, 2006, entitled "High-Aluminum Alloy For General Galvanizing", which applications are hereby incorporated by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to compositions and processes for the production of high-aluminum alloy. More specifically the patent relates to compositions and processes for the production of high-aluminum alloy for general galvanizing. In one embodiment, the present invention relates to a unique combination of a zinc-ammonium flux and a molten zinc-aluminum alloy bath containing silicon. The present invention also relates to an improvement in the fluxing step used in the galvanizing process for steel, and high aluminum-content coated steel made using that improved process.

BACKGROUND OF THE INVENTION

[0003] The importance of providing protection against corrosion for steel articles used outdoors (such as fences, garbage cans, and automobile parts) is obvious, and coating the steel with zinc is a very effective and economical means for accomplishing this end. Zinc coatings are commonly applied by dipping or passing the article to be coated through a molten bath of the metal. This operation is termed "galvanizing," "hot galvanizing" or "hot-dip galvanizing" to distinguish it from zinc electroplating processes. The steel galvanizing process is very well-known in the art and, for example, is discussed in detail in The Making, Shaping, and Treating of Steel, United States Steel Corporation, 7th Edition, Pittsburgh, 1957, pages 660-673, and

the 10th edition, Lankford et al. (eds.), Association of Iron and Steel Engineers, Pittsburgh, 1985, pages 1173-1189, incorporated herein by reference. Galvanization processes generally fall into one of two types: (1) batch hot-dip galvanizing, which is the hot-dip galvanizing of pre-formed articles by passing them one by one and in close succession through the molten zinc, and (2) continuous (strip) hot-dip galvanizing, in which steel in coiled form from the rolling mills is uncoiled and passed continuously through the galvanizing equipment, continuity of operation being achieved by joining the trailing end of one coil to the leading end of the next.

[0004] Earlier, we presented a new alloy system for general galvanizing, which consisted of zinc with around 23 wt.-% Al. This is the eutectoid composition as can be seen in Figure 1. Slow cooling of the eutectoid composition would theoretically produce a lamellar two-phase structure of the phases with 32 wt.-% and 99 wt.-% zinc. The idea behind this development project was that zinc-Al alloys with the eutectoid composition are known to be ductile [1,2]. Eutectoid structures are very fine lamellar two-phase systems. A well-known example is pearlite in steel, which is a ferrite-cementite eutectoid lamellar composition. A 78-22 wt.-% superplastic Zn-Al alloy is commercially available under the name Prestal®.

[0005] There is a need, however, to combine good formability with the enhanced corrosion protection However, gigantic hurdles had to be overcome before such an alloy coating could be introduced into the general galvanizing industry. Some of the difficulties encountered were the following:

1. High-Al alloys cannot be produced using the standard zinc-ammonium chloride flux. A flux based on Cu and Sn had been proposed earlier, but the possibility of copper leaching into the zinc bath is not an attractive one. Better fluxes are needed.

2. High-Al alloys have a tendency to form outbursts of zinc-iron intermetallics that are formed at a later stage in the galvanizing process, i.e., after iron-aluminum intermetallics have already been formed [3]; these are caused by diffusion of zinc atoms

into the grain boundaries of the iron-aluminum alloys which have become unstable in the later stage of immersion and breaks down. The liquid zinc reaches the iron which, at that temperature, leads to an almost explosive reaction with formation of large amounts of iron-zinc alloy, the outbursts. This phenomenon leads to very thick, uncontrolled and rough coatings. Control of the outbursting effect is absolutely essential before this alloy can become commercially viable.

3. Wettability issues were previously reported. Zn-Al alloys seem to have a higher surface tension than pure zinc, hence bare spots due to poor wetting of the steel are easily formed. Additives needed to be found that would lower the surface tension of the melt. This issue may also be related to the flux that is used for this alloy.

4. A poor control of thickness of the coating was reported. It seemed to depend on the temperature, the flux, the dipping time, the steel quality and other factors. At the time of the first presentation on this alloy, these factors were not known very well and more systematic studies were needed.

5. A number of additional unanswered questions remained, such as the amount of bottom dross and top dross formed by this bath as well as the concentration of iron that would develop over time. The iron solubility could be affected by the high aluminum content, but no literature information on this aspect is available. It is known, though, that the iron solubility in pure zinc increases strongly with temperature, and that the increased solubility results in larger amounts of bottom dross formation in baths that are run at higher temperatures, for instance the so-called delta-galvanizing process [4].

6. The liquidus of the Zn23Al0.3Si alloy is 482°C (Figure 1) hence the galvanizing temperature has to be at least 530°C or even higher. This implies that the new alloy can only be run in ceramic kettles, unless it can be demonstrated that the high-Al bath is considerably less corrosive to kettle steels than baths of

pure zinc.

7. In the study of the above issues, it was found that there is no relevant literature on the use of the Zn23Al0.3Si alloy for batch galvanizing. The existing literature on other Zn-Al alloys, e.g., Galvalume® and Galfan®, is not relevant. Galvalume® is a continuous product and Galfan®, even the batch version is different in flux, Al content, melting point, reactivity and other aspects.

[0006] The galvanizing process and materials were developed, such as bath composition, bath temperature, dipping time and flux composition, so that a wide range of steel compositions could be galvanized successfully. The flux was a modified zinc-ammonium chloride flux. The problem of localized intermetallic outbursts that develop when galvanizing with high-Al baths, was solved by the addition of 0.3-0.5 wt.-% Si to the bath. Data will be presented on the microstructure, mechanical properties and corrosion resistance of the new coating. The coating consists of only two layers, a thin uniform layer of iron aluminides at the steel-coating interface, and a drag-out layer which has the overall bath composition, which separates into a fine eutectoid primary structure and a coarser eutectic secondary phase during cooling. The coatings are hard yet ductile, and in electrochemical tests the corrosion rate is a factor 5 lower than for conventional HDG. The salt spray resistance (first appearance of red rust) is a factor 6 better than that of conventional zinc coatings (350 hrs vs. 2000 hrs). The corrosion resistance is also considerably better than that of Zn5Al. The coating provides outstanding cathodic protection despite the high Al content. This is attributed to the fact that the Al is not passive but remains active at all times. The thickness of the new coating, which can be dipped in the wide temperature range of 510-600°C, is in the range of 10-30 μm depending on dipping time, which makes this new system very attractive for use on fasteners. Other important aspects of this new system are: i) the bath does not form bottom dross, and ii) the Sandelin effect is absent in this process: practically equivalent coatings

were obtained with cold-rolled or hot-rolled steels varying in silicon content by a factor of 11 (a range of 0.03 to 0.35 wt.-%).

[0007] The present invention investigated whether the addition of silicon could stabilize the iron-aluminum intermetallic layer, thus preventing outbursting effects. Silicon is used in Galvalume® at the level of 1.5 wt.-% for that purpose [5]. Another objective was to develop a new flux for this high-Al alloy that would eliminate the copper-tin flux used previously.

[0008] REFERENCES

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BRIEF SUMMARY OF THE INVENTION

[0009] The present invention relates to a novel alloy that has been developed for general galvanizing purposes. The present invention provides for a solution to the pressure by several European governments on zinc suppliers and galvanizers to reduce the run-off of zinc into the environment from galvanized parts, including guard rails on highways, lamp posts, fences, etc. Thus, the main focus was to develop an alloy system that has a higher corrosion resistance than regular hot-dipped zinc coatings when exposed to various atmospheres. Therefore, the potential of adding aluminum to the zinc bath at a level of about 23 wt.-% was studied. Such Zn-Al alloys are known to have a much higher atmospheric corrosion resistance than pure zinc. The major obstacles in this R&D project were two-fold; a) a flux had to be developed that is compatible with high-Al zinc baths; b) at the galvanizing temperatures of 500°C and higher Al is much more reactive to steel than zinc. The result of this effect is the so-called outbursting effect, a known phenomenon for high-Al baths. Both problems were solved, however, and the alloy can now be made reproducibly on a wide range of structural steels using a simple flux method. The copper-tin flux has been eliminated and a modified zinc ammonium chloride flux has been shown to work well. Previous assumptions that such fluxes are incompatible with high-Al baths were unfounded.

[0010] The metal component to be coated is typically dipped into the allow composition for at least 1 minute. In one embodiment, the metal component to be coated is dipped into the allow composition for 1-10 minutes. In another embodiment, the metal component to be coated is dipped into the allow composition for 1-8 minutes. In another embodiment, the metal component to be coated is dipped into the allow composition for 2-6 minutes. In another embodiment, the allow composition is at least 500, 510, 515, 520, or 525°C. In another embodiment, the allow composition is less than 650, 630, 625, 620,

610, or 600°C. The typical dipping conditions of this new alloy are 2-5 minutes at 500-650°C, depending on the thickness of the part.

[0011] Both cold-rolled and hot-rolled steels can be galvanized. The metal coating bath contains only one additive other than zinc and aluminum, *viz.*, silicon. This additive suppresses the outbursting effect effectively if used in the range of 0.2-0.9 wt.-%. With time the Si concentration remains fairly constant. It can be replenished by adding a master alloy of Zn23Al2Si together with the other master alloy Zn23Al. Typical galvanizing additives such as lead, tin, bismuth, nickel, vanadium, rare earth metals or others are not required.

[0012] In one embodiment, the alloy further comprises 0.001-0.6% by weight nickel. In another embodiment, the alloy further comprises 0.001-0.6% by weight vanadium.

[0013] Among the main results are that the formation and properties of the new alloy coating are independent of the silicon content of the steel. A range of silicon contents spanning a factor of 11 have been tested. Thus, the so-called Sandelin effect, notorious in general galvanizing, has been eliminated.

[0014] In one embodiment, the thickness of the coating is about 20-60 μm, i.e., considerably less than the currently used galvanized coatings. In one embodiment, the thickness of the coating is about 25-30 μm. In one embodiment, the coating has a simple structure consisting of an interfacial iron-aluminum layer (mainly Fe_2Al_5 or $Fe_{2-x-y}Al_5Zn_xSi_y$) at the steel-coating interface and a drag-out layer of approximately the bath composition. It is the iron-aluminum layer that provides an extraordinary corrosion resistance to the steel. Upon cooling the top layer separates into several phases, with the exact composition depending somewhat on the type of steel and on the cooling rate. The relative thickness of the two layers has a slight temperature dependence. At very high galvanizing temperature (e.g., 600°C), the ratio of base layer to top layer is 10/20 μm, whereas at 510°C, which is the lowest temperature that gave good-quality coatings, the thicknesses were 5/25 μm, typically. This example shows that the temperature of the bath is not critical in this new process. Further, it demonstrates that

the steel is very well passivated by the iron-aluminum alloy. The base layer does not grow linearly with time or exponentially with temperature. An important implication of this observation could be that certain steel kettles could possibly also run this alloy system and not just ceramic kettles. This expectation is based on the strong passivation of the steel by the bath due to the $Fe_{2-x-y}Al_5Zn_xSi_y$ layer and the lack of further growth with time. The very low equilibrium iron content in the bath is another indication that this alloy might have much wider applicability than previously thought. However, this supposition needs to be verified by experimental data, which we will collect in the near future.

[0015] It is important to note that this bath does not form bottom dross, so the work flow does not have to be interrupted for drossing. The amount of top dross is also very low, and there is almost no dissolved iron in the bath. From a corrosion standpoint, the new alloy of 30 μm thickness lasts for at least 2000 hours in the salt spray chamber as opposed to 350 hours for a regular zinc coating. Electrochemical tests indicated a factor of 5 better corrosion resistance compared to conventional HDG coatings in a dilute salt electrolyte and 3 times better than the Zn5Al coating. The cathodic protection in a scribe is excellent and again outperforms regular hot-dip coatings and Zn5Al. This result was explained on the basis of the absence of passivation of the aluminum in the alloy. Electrochemical data confirmed this assumption. The hardness of the coating is much higher than those of regular zinc coatings, yet the coatings are ductile.

[0016] In one embodiment, the Zn23Al0.3Si bath has to be run at considerably higher temperatures than conventional batch galvanizing, viz., ≥510°C vs. 450°C. However, what one gets in return for the higher heating costs is a coating that at only 1/3 of the coating thickness of current HDG, exhibits a performance in many tests that is considerably better, *e.g.*, a factor of 6-7 in salt spray resistance and other tests.

[0017] In one embodiment of the invention, the present inventors have noted the marked cleaning effect of molten zinc chloride on an iron or steel

material (hereunder often simply referred to as "a steel material") and found that a smooth and beautiful galvanized film of a zinc-aluminum alloy could be formed on the surface of a steel material by a method in which a steel material that was freed of an oxide film by ordinary preliminary treatments such as degreasing and pickling was immersed in a zinc chloride based, aqueous flux bath in an independent vessel, withdrawing the steel material from the flux bath and subsequently dipping it in a molten zinc-aluminum bath in a separate galvanizing vessel. The present inventors also found a flux composition suitable for use in the practice of the method. In one embodiment, the flux is G Flux, which can be purchased from Teck Cominco in Mississauga, Canada, under the name of Aluflux.

[0018] Aluflux is described more fully in United States Provisional Patent Application No. 60/751,660, filed December 20, 2005, entitled "Flux and Process For Hot Dip Galvanization", and United States Provisional Patent Application No. 60/810,173, filed June 2, 2006, entitled "Flux and Process For Hot Dip Galvanization", the entire contents of which applications are incorporated herein by reference.

[0019] Thus, in one embodiment, the present invention provides a method of galvanizing with a molten zinc-aluminum alloy by immersing an oxide-film free steel material in a molten G Flux bath in an independent vessel and thereafter immersing the flux coated steel material in a molten zinc-aluminum alloy bath in a separate vessel to be coated with a zinc-aluminum alloy layer.

[0020] In another embodiment, the flux bath comprises at least one metal chloride selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides, and the balance being zinc chloride.

[0021] In another embodiment, the metal chloride is ammonium chloride and is present at a concentration of 200 to 800 g/L (100-300 g/L ammonium) where the ammonium accounts for about 10 to about 30 wt % of the flux bath. In another embodiment, the ammonium accounts for about 1 to about 25 wt % of the flux bath. In another embodiment, the ammonium accounts for about 1 to about 15 wt % of the flux bath

[0022] In a further embodiment, the flux bath comprises additional additives comprising one or more of iron, nickel, cobalt, boron, carbon, chromium, molybdenum, manganese, tungsten, and silicon.

[0023] In one embodiment, the flux is an aqueous flux for hot dip galvanization comprising from about 10 to 40 weight % zinc chloride, about 1 to 15 weight % ammonium chloride, about 1 to 15 weight % of an alkali metal chloride, a nonionic surfactant and including an acidic component such that the flux has a final pH of about 1.5 or less.

[0024] In one embodiment, the flux is an aqueous flux for hot dip galvanization comprising from about 15 to 40 weight % zinc chloride, about 1 to 10 weight % ammonium chloride, about 1 to 6 weight % of an alkali metal chloride, a surfactant and including an acidic component such that the flux has a final pH of about 1.5 or less.

[0025] The flux composition according to the invention generally comprises at least one surfactant. This is advantageously an anionic and/or nonionic surfactant. It can also be a cationic, amphoteric or zwitterionic surfactant.

[0026] Among the anionic surfactants which may be mentioned in particular are soaps such as salts of C8 -C24 fatty acids, for example salts of fatty acids derived from coconut and from tallow; alkylbenzenesulfonates, in particular alkylbenzenesulfonates of a linear C8 -C13 alkyl in which the alkyl group comprises from 10 to 16 carbon atoms, alcohol sulfates, ethoxyalted alcohol sulfates, hydroxylalkyl sulfonates; alkyl sulfates and sulfonates, in particular of C12 -C16 alkyl, monoglyceride sulfates, and condensates of fatty acid chlorides with hydroxyalkylsulfonates.

[0027] Among the nonionic surfactants which may be mentioned in particular are alkylene oxide condensates, in particular condensates of ethylene oxide with alcohols, polyols, alkylphenols, fatty acid esters, fatty acid amides and fatty amines; amine oxides, sugar derivatives such as alkylpolyglycosides or fatty acid esters of sugars, in particular sucrose monopalmitate; long-chain tertiary phosphine oxides; dialkyl sulfoxides; block copolymers of polyoxyethylene and of

polyoxypropylene; alkoxylated sorbitan esters; fatty esters of sorbitan, poly(ethylene oxides) and fatty acid amides modified so as to give them a hydrophobic nature (for example fatty acid mono- and diethanolamides containing from 10 to 18 carbon atoms).

[0028] In one embodiment, the surfactant may be one or more of polyoxyalkylenated (polyethoxyethylenated, polyoxypropylenated or polyoxybutylenated) alkyl phenols in which the alkyl substituent is C6 -C12 and containing from 5 to 25 oxyalkylene units; by way of example, mention may be made of Triton X-45, X-114, X-100 or X-102 sold by Rohm & Haas Co.; glucosamides, glucamides and glycerolamides; polyoxyalkylenated C8 -C22 aliphatic alcohols containing from 1 to 25 oxyalkylene (oxyethylene or oxypropylene) units. By way of example, mention may be made of Tergitol 15-S-9 and Tergitol 24-L-6 NMW sold by Union Carbide Corp., Neodol 45-9, Neodol 23-65, Neodol 45-7 and Neodol 45-4 sold by Shell Chemical Co., and Rhodasurf IDO60, Rhodasurf LA90 and Rhodasurf IT070 sold by the company Rhodia; amine oxides such as (C10 -C18)alkyldimethylamine oxides and (C8 -C22) alkoxyethyldihydroxyethylamine oxides; the alkyl polyglycosides described in U.S. Pat. No. 4,565,647; C8 -C20 fatty acid amides; ethoxylated fatty acids; ethoxylated amines.

[0029] Among the preferred nonionic surfactants which may be mentioned are surfactants such as polyoxyethylenated C6 -C12 alkoylphenols, polyoxyethylenated and/or polyoxypropylenated C8 -C22 aliphatic alcohols, ethylene oxide/propylene oxide block copolymers, optionally polyoxyethylenated carboxylic amides, etc. They also comprise from 0% to 10% and preferably from 0.005% to 5% by weight, relative to the total weight of the composition.

[0030] The flux formulations can also contain other additives, in particular other surfactants, such as: nonionic surfactants such as amine oxides, alkylglucamides, oxyalkylenated derivatives of fatty alcohols, alkylamides, alkanolamides and amphoteric or zwitterionic surfactants, etc. as already mentioned above.

[0031] Surfactants that are preferred are nonionic surfactants, in particular the compounds produced by condensation of alkylene oxide groups as described above which are of hydrophilic nature with a hydrophobic organic compound which may be of aliphatic or alkyl aromatic nature.

[0032] The length of the hydrophilic chain or of the polyoxyalkylene radical condensed with any hydrophobic group may easily be adjusted to obtain a water-soluble compound which has the desired degree of hydrophilic/hydrophobic balance (HLB).

[0033] Exemplary nonionic surfactants include: alkylphenol type surfactants represented by R--C6 H4 --O-- (CH2 CH2 O)n H (n=2-50; R is an alkyl group having a straight chain or a simple side chain (Cx H2x+1, X=1-20)); preferably, R=C9 H19 or C8 H17 ; a higher alcohol type surfactants represented by RO(R'O)n (R"O)m H (HLB value=7-16; R is an alkyl group having a straight chain or a simple side chain, R' and R" are an alkylene group having a straight chain or a simple side chain (Cx H2x, x=1-20); n=1-30, m=1-30); and polyalkylene glycol type surfactants represented by RO(EO/PO)n H (R is an alkyl group having a straight chain or a simple side chain; E=CH2 CH2 ; P=CH2 CH2 CH2 ; n=1-50). Exemplary water-soluble polymers include polyethylene glycol and polyvinyl alcohol.

[0034] Examples of commercially available nonionic surfactants are Plurafac LF401 (manufactured by BASF), Tetronic TR-702 (manufactured by Asahi Denka Kogyo Co., Ltd.), Naimeen L-207 (manufactured by Nippon Oil and Fats Co., Ltd.), Liponox NC-100 (Lion Co., Ltd.), and the like.

[0035] In one embodiment, the nonionic surfactants are characterized as alkoxylated surfactants including compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which exhibits water insolubility has a molecular weight of from about 1,500 to 1,800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the product is retained up to the point where polyoxyethylene content is about 50 percent of

the total weight of the condensation product. Examples of such compositions are the "Pluronics" sold by BASF.

[0036] Other suitable nonionic surfactants include those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene-diamine or from the product of the reaction of a fatty acid with sugar, starch or cellulose. For example, compounds containing from about 40 percent to about 80 percent polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, and hydrophobic bases having a molecular weight of the order of 2,500 to 3,000 are satisfactory.

[0037] In addition, the condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide and propylene oxide, e.g., a coconut alcohol-ethylene oxide--propylene oxide condensate having from 1 to 30 moles of ethylene oxide per mole of coconut alcohol, and 1 to 30 moles of propylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms, may also be employed.

[0038] In one embodiment, the surfactant may be one or more of alkoxylated alcohols which are sold under the tradename of "Polytergent SL-series" surfactants by Olin Corporation or "Neodol" by Shell Chemical Co.

[0039] The polycarboxylated ethylene oxide condensates of fatty alcohols manufactured by Olin under the tradename of "Polytergent CS-1" are believed to be the most effective anionic surfactants. Polytergent CS-1 in combination with the above Polytergent SL-Series surfactants have been found particularly effective.

[0040] Effective surfactants which also provide antifoam properties include "Polytergent SLF-18" also manufactured by Olin and "Surfonic LF37" by Texaco which are nonionic alkoxylated alcohols.

[0041] In one embodiment, the flux is an aqueous flux for hot dip galvanization comprising from about 15 to 40 weight % zinc chloride, about 1 to 10 weight %, preferably about 1 to 6 weight %, ammonium chloride, about 1 to 6 weight % of an alkali metal chloride, about 0.02 to 0.1 weight % of a nonionic surfactant containing, polyoxyethylenated straight-chain alcohols with a hydrophile-lipophile balance (HLB) of less than 11, and including an acidic component so that the flux has a pH of about 1.5 or less.

[0042] According to another aspect of the invention, the flux is an aqueous flux for hot dip galvanization comprising from about 15 to 40 weight % zinc chloride, about 1 to 10 weight %, preferably about 1 to 6 weight %, ammonium chloride, about 1 to 4 weight % ferric chloride, about 1 to 6 weight % of an alkali metal chloride, about 0.02 to 0.1 weight % of a nonionic surfactant containing polyoxyethylenated straight-chain alcohols with a hydrophile-lipophile balance (HLB) of less than 11, about 0.1 to 0.2 weight % of an inhibitor containing an amino derivative, and including an acidic component so that the flux has a pH of about 1.5 or less.

[0043] According to another aspect of the invention, the flux may further comprise bismuth, such as in the form of bismuth oxide, or other suitable bismuth compound, such as bismuth chloride or bismuth oxychloride. The flux may contain Bi_2O_3 in an amount of at least about 0.02 weight % Bi_2O_3 or more, preferably about 0.05%.

[0044] According to another aspect of the invention, the flux comprises from about 15 to 40 weight % zinc chloride, about 1 to 10 weight % ammonium chloride, about 1 to 6 weight % of an alkali metal chloride, about 0.02 to 0.1 weight % of a nonionic surfactant containing polyoxyethylenated straight-chain alcohols with a hydrophile-lipophile balance (HLB) of less than 11, and including an acidic component so that the flux has a pH of about 1 5 or less.

[0045] According to another aspect of the invention, the flux comprises from about 15 to 40 weight % zinc chloride, about 1 to 10 weight % ammonium chloride, about 1 to 4 weight % ferric chloride, about 1 to 6 weight % of an alkali metal chloride, about 0.02 to 0.1 weight %

of a nonionic surfactant containing, polyoxyethylenated straight-chain alcohols with a hydrophile-lipophile balance (HLB) of less than 11, about 0.1 to 0.2 weight % of an inhibitor containing an amino derivative, and including an acidic component so that the flux has a pH of about 1.5 or less. In one embodiment, the surfactant is MERPOL™ SE.

[0046] In one embodiment, the molten zinc-aluminum alloy bath is an aluminum-zinc alloy containing at least 10, 15, 16, 17, 18, 19, 20, 21, 22, or 23% by weight of Al and at least 0.18, 0.2, 0.25, 0.3, 0.35 or 4% by weight of silicon. In one embodiment, the molten zinc-aluminum alloy bath is an aluminum-zinc alloy containing 10%-40% by weight of Al and 0.2%-0.9% by weight of Si and the remainder is zinc. In one embodiment, the molten zinc-aluminum alloy bath is an aluminum-zinc alloy containing 20%-25% by weight of Al and 0.2%-0.7% by weight of Si and the remainder is zinc.

[0047] In a further embodiment, the aluminum accounts for about 10 to about 40 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the aluminum accounts for about 20 to about 25 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the aluminum accounts for about 22 to about 24 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the aluminum accounts for about 23 wt % of the molten zinc-aluminum alloy bath.

[0048] In a further embodiment, the silicon accounts for about 0.18 to about 0.75 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the silicon accounts for about 0.2 to about 0.7 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the silicon accounts for about 0.3 to about 0.5 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the silicon accounts for about 0.3 wt % of the molten zinc-aluminum alloy bath.

[0049] In a further embodiment, the metal layer has a thickness of from about 1 nm to about 10 μm. In a further embodiment, the fluxing step is carried out for from about 1 to about 10 minutes, at a temperature of from about room temperature to about 100°C. In another embodiment, the fluxing step is carried out at a temperature of from about 20°C to

about 50°C. In another embodiment, the fluxing step is carried out at a temperature of from about 22°C to about 35°C. In another embodiment, the metal is selected from the group consisting of low carbon steels, ultra-low carbon steels, titanium steels, chromium steels and stainless steels.

[0050] In another embodiment, the galvanizing step is carried out for from about 1 to about 5 minutes at a temperature of from about 500°C to about 600°C. In another embodiment, the galvanizing step is carried out for from about 2 minutes to about 3 minutes at a temperature of from about 510°C to about 530°C. In another embodiment, prior to fluxing, the article is degreased by dipping it in an alkaline solution and is pickled by dipping it in an acid solution.

[0051] In one embodiment of the present invention, the molten flux bath and the molten zinc alloy bath are held in separate vessels, so the temperatures of the two baths can be controlled independently of each other. The temperature of the molten flux bath in an independent vessel must be higher than the melting point of the flux composition. In one embodiment, the range of the temperature of the molten flux bath is between 400 and 600°C. In another embodiment, the range of the temperature of the molten flux bath is between 500 and 600°C. In another embodiment, the range of the temperature of the molten flux bath is between 510 and 600°C. In another embodiment, the range of the temperature of the molten flux bath is between 510 and 550°C.

[0052] The temperature of the molten zinc-aluminum alloy bath in a separate dip galvanizing vessel is generally from about 400 to about 650°C. In one embodiment, the temperature of the molten zinc-aluminum alloy bath is from about 500 to about 650°C. In another embodiment, the temperature of the molten zinc-aluminum alloy bath is from about 500 to about 625°C. In another embodiment, the temperature of the molten zinc-aluminum alloy bath is from about 550 to about 625°C.

[0053] Examples of the steel material to be galvanized by the galvanizing method of the invention include low carbon steels, ultra-low carbon steels, titanium steels, chromium steels and stainless steels. The galvanizing method of the invention is applicable not only to steel

structures or related components thereof, but also to sheets, tubes and wires; therefore, the applicability of the invention method covers both batch-wise and continuous operations.

[0054] The present invention relates to an improvement in the fluxing step used in the galvanizing process for steel, and high aluminum-content steel made using that improved process. Such galvanizing processes, in general, are well-known and fully described in the art; they consist generally of two types: continuous galvanization and batch galvanization. See, for example, The Making, Shaping and Treating of Steel, United States Steel Corporation, 7th Edition, 1957, Pittsburgh, Chapter 39, pages 660-673, 1957, and the 10th edition, Lankford et al. (eds.), Association of Iron and Steel Engineers, Pittsburgh, 1985, pages 1173-1189, incorporated herein by reference. The improvement of the present invention is useful in any galvanizing process, but is especially useful in batch galvanization processes for steel where there is frequently a significant time delay between the fluxing of an article and the actual galvanization of that article.

[0055] In a typical batch galvanization process, the surface of the article to be galvanized is treated to remove rust and other foreign materials, the article is then fluxed and, finally, it is dipped in molten zinc to provide the galvanization. The surface preparation steps (i.e., degreasing and pickling) utilized in the process of the present invention are conventional and are known in the art. The purpose of these steps is to remove rust and other foreign materials from the surface of the steel article. This is generally accomplished by a degreasing step (to remove organic contaminants from the steel surface) in which the article is dipped in a heated alkaline solution. In a typical degreasing step, the steel article is dipped for about 5 to about 60 minutes in an alkaline solution containing sodium hydroxide and sodium orthosilicate in a weight ratio of about 1:1, and a concentration of 10 to 15%, at a temperature of about 60°C to about 80°C Other alkaline materials, such as potassium hydroxide, can be used. After this degreasing step is completed, the steel article is generally rinsed with water to remove the

alkaline solution and any foreign substances (e.g., dirt and other organic particles) sticking to its surface.

[0056] This is typically followed by a pickling step (to remove mill scale and rust from the steel surface) wherein the steel article is dipped in an acid solution, preferably one containing hydrochloric acid or sulfuric acid. Pickling for sheet galvanizing is usually conducted as a batch operation in stationary tubs provided with an agitating means. This operation may sometimes be conducted as a continuous process in equipment provided with a sheet conveyor and means for electrolytic acceleration. Very light pickling, requiring only a short time exposure to the pickling solution, has been found suitable for products, such as roofing and siding, that require little mechanical deformation. Deep etching (i.e., heavy pickling) of the base metal has generally been found to be necessary when forming requirements are severe. The pickling is generally accomplished by dipping the article for as long as 5 to 30 minutes in a 10 to 15% aqueous solution of sulfuric acid (or hydrochloric acid), containing about 0.5% to about 0.7% of a pickling inhibitor, at room temperature or a temperature of about 50°C to about 70°C Higher bath temperatures require shorter immersion times. Typically, after the pickling step is concluded, the article is rinsed with water to remove excess pickling solution and iron salts sticking to the steel surface. The result of these processes is an object having a very active surface, since all the rust and other foreign materials have been removed, making it highly susceptible to oxidation.

[0057] In accordance with another embodiment of the invention, bismuth, antimony, nickel, zinc, aluminum, chromium, titanium, tin, copper, iron and/or magnesium are added to the metal alloy coating to enhance the physical properties of the metal alloy, improve corrosion resistance, improve grain refinement, inhibit oxidation, inhibit dross formation during coating, stabilize the metal alloy, and/or inhibit the crystallization of the tin in tin containing metal alloys. In one embodiment, the metal alloy coating is an alloy primarily including tin for a single phase coating alloy system or primarily including tin and zinc for a two-phase alloy system. In one embodiment, the metal alloy

contains metal stabilizing additives. When tin crystallizes, the bonding of the tin containing alloy coating to the metal strip weakens and results in flaking of the coating. The addition of small amounts of stabilizing metals, such as bismuth, antimony, copper and mixtures thereof in an amount of at least 0.005 weight percent prevents and/or inhibits the crystallization of the tin. For two-phase tin and zinc alloy coatings, the amount of metallic stabilizer required to inhibit the crystallization of the tin in the two-phase alloy may be as low as 0.005. In one embodiment, for a single phase tin alloy coating, the amount of metallic stabilizer in the alloy should be at least 0.01 weight percent. Bismuth and/or antimony also enhances the hardness, strength, mechanical properties and corrosion resistance of the metal alloy coating. Nickel, as a small additive, has been found to provide additional corrosion protection to the two-phase tin and zinc alloy coating especially in alcohol containing environments, such as for gasoline tanks. Copper can be added to single phase tin alloy coating systems and two-phase tin and zinc alloy coating systems, in addition to its stabilizing properties, as a coloring agent to reduce the reflective properties of the newly applied metal alloy and/or to obtain the desired coloring of the weathered metal alloy coating. Copper also improves the corrosion-resistance of the metal alloy coating especially in marine environments. Magnesium, when added in small amounts, has been found to improve the flow or coating properties of a two-phase tin and zinc alloy system so that more uniform coating is applied to the metal material. Magnesium also reduces the anodic characteristics of the coating to further increase the corrosion-resistance of the metal alloy coating. The magnesium also reduces oxidation of the molten metal alloy and/or reduce dross formation during the coating of the metal alloy. Aluminum is added to a single phase tin alloy system and to a two-phase tin and zinc alloy system in amounts of less than about 5 percent by weight of the coating alloy to inhibit oxidation of the molten metal alloy and to reduce dross formation on the metal alloy coating. Aluminum also reduces the thickness of the intermetallic Fe--Zn layer resulting from zinc containing metal alloys so as to improve the formability of the coated metal material. Titanium is added to a

two-phase tin and zinc alloy system, in small amounts, to improve the grain refinement of the coated metal alloy and to increase the hardness and the strength of the metal alloy. Titanium also prevents oxidation of the molten metal alloy and helps reduce dross formation.

[0058] In one embodiment, a metal coloring agent is added to the metal alloy to alter the reflective properties of the newly applied metal alloy. By adding a coloring agent such as metallic copper to the metal alloy, the newly coated strip exhibits a duller, less reflective surface. Metallic cooper adds a reddish tint to the metal alloy which significantly reduces the light reflective properties of the coating. Copper also assists in the corrosive resistive properties of the metal alloy. Copper is also added for its stabilizing properties for tin.

[0059] In one embodiment, zinc metal is added to further increase the hardness of the tin based alloy while also contributing to the corrosion resistance of the metal alloy.

[0060] In one embodiment, the thickness of the metal strip is not more than about 0.2 inch. In one embodiment, it is less than 0.05 inch, less than 0.03 inch and greater than 0.005 inch. A "strip" is defined as metal that is shipped to the coating process in coils, as opposed to plates. In addition, obtaining heat or temperature equilibrium of the strip during hot-dipping to properly form an intermetallic layer between the strip surface and coating alloy is very difficult with a thick strip at high speeds. Strip thicknesses which are less than 0.005 inch may break as the strip passes at high speeds and/or are under tension when being passed through the molten coating alloy. The thickness of the strip is also selected so that the formed or drawn coated strip is strong and durable enough for its intended end purpose. When stainless steel strip is used, 304 or 316 stainless strip having a thickness of 0.005-0.03 inch is used in one embodiment.

[0061] In one embodiment, the metal to be coated is heated in a reducing atmosphere to reduce oxidation. In one embodiment, the metal is heated in a reducing atmosphere after pretreatment. In one embodiment, the pretreatment is cleaning and/or pickling of the metal.

[0062] The reducing atmosphere is not critical as long as it is a reducing atmosphere. In one embodiment, N_2 gas containing at least 0.5% of H_2 or H_2 gas can be used, with N_2 gas containing 1 to 20%, typically about 5% of H_2 is used.

[0063] It is known that the oxide layer on steel strip may contain Fe2 O3, Fe3 O4, and/or FeO, or various ratios of the three oxide forms depending on the conditions in which the product is made and conducted to the next processing stage. Fe3 O4 may pass through the Fe2 O3 stage before it is further reduced to FeO and then completely reduced to iron.

[0064] Where hydrogen is the reducing agent, water is produced; where carbon is the reducing agent, carbon monoxide is first produced, and where carbon monoxide is the reducing agent, carbon dioxide results. The present invention contemplates the use of either hydrogen or carbon monoxide, or any other commercially feasible reducing gas, in the absence of or together with elementary carbon as a supplementary reductant.

[0065] Further, the hydrogen may be manufactured within the enclosure or in its immediate vicinity. Examples of the manufacture of hydrogen include known processes for accomplishing the dissociation of methane, and the combustion of methane or other hydrocarbons in such a way as to produce excess hydrogen.

[0066] In another embodiment, the coating obtained on wires, tubes and strips is produced in a continuous process, which can have substantially the same thickness and corrosion performance to the coating obtained in the batch process, despite the difference in contact time, viz., about 2 s instead of about 2 min. This process is obtained by lowering the silicon content of the bath significantly. The low silicon content increases the reactivity of the aluminum in the bath for the steel, so that in 2 s a substantial amount of iron-aluminum alloy can be formed. It is that alloy that gives Aleutec the enormous corrosion resistance.

[0067] In another embodiment, the coating is used for highway guard rails, automobile fuel tanks, rebar, fasteners, and other similar metals.

[0068] In another embodiment, the method comprises dipping the metal object into the liquid bath for about 2 s wherein the steel is first deoxidized in a reducing atmosphere. In one embodiment, the reducing atmosphere comprises hydrogen, natural gas, or mixtures thereof. In another embodiment, the steel has substantially the same temperature as the bath. This is done for metal strips and tubes. In one embodiment, the bath composition comprises about 23% Al and about 0.03-0.1 % Si. For the batch process (2 min dipping), the bath comprises about 23% Al and about 0.3-0.7 % Si.

[0069] In another embodiment, the problem of localized intermetallic outbursts that develop when galvanizing with high-Al baths is solved by the addition of 0.3-0.5 wt.% Si to the bath. In one embodiment, the bath comprises 0.1 - 0.9 wt.% Si. In another embodiment, the bath comprises 0.3 - 0.7 wt.% Si. In another embodiment, the bath comprises 0.4 - 0.6 wt.% Si.

[0070] In one embodiment, there is provided a metal strip of stainless steel, carbon steel or copper coated with a corrosion-resistant metal alloy. In one embodiment, the metal coating alloy is an alloy primarily including tin for a single phase alloy system or primarily including tin and zinc for a two-phase alloy system. Other metal strip compositions which may be coated include metal strip made of nickel alloys, aluminum, titanium and bronze. "Stainless steel" in the application is used in its technical sense and includes a large variety of alloy metals containing chromium and iron. Chromium plated ferrous materials are also stainless steel. During hot-dipping, the plated chromium softens and intermingles with the ferrous strip to form a ferrous-chromium alloy. The stainless steel may also contain other elements such as nickel, carbon, molybdenum, silicon, manganese, titanium, boron, copper, aluminum and various other metals or compounds. Elements such as nickel can be flashed (electroplated) onto the surface of the chromium-iron alloy or directly incorporated into the chromium-iron alloy, i.e. the stainless steel.

[0071] In accordance with another aspect of the present invention, the metal strip is plated, metal spayed or hot dipped with an intermediate metal

barrier prior to applying the metal alloy coating to the strip surface. The intermediate metal barrier provides additional corrosion resistance, especially against halogens such as chlorine. The metal barrier preferably is tin, nickel, copper or chromium. Other metals such as aluminum, cobalt, molybedum, Sn--Ni or Fe--Ni are also used. The metal barrier is applied to the metal strip to form a very thin metal layer. Although the metal alloy coating provides excellent protection against most corrosion-producing elements and compounds, and forms a strong bond with the metal strip, the inclusion of the intermediate metal barrier enhances the bonding and/or corrosion resistant characteristics of the metal coating alloy. The nickel is preferably flashed or plated to the metal strip surface. Nickel plating of the metal strip has been found to improve corrosion-resistance especially against compounds such as chlorine which have the ability to penetrate the metal alloy coating and attack and oxidize the surface of the metal strip thereby weakening the bond between the metal strip and the metal alloy coating. The nickel barrier has been found to provide an essentially impenetrable barrier to these elements and/or compounds which in fact penetrate the metal alloy coating. Due to the very small amount of these compounds penetrating the metal alloy coating, the thickness of the nickel barrier is preferably maintained at an ultra-thin thicknesses while still maintaining the ability to prevent these components from attacking the metal strip. The metal alloy coating and thin nickel coating effectively complement one another to provide superior corrosion resistance. Tin, chromium or copper form an intermediate metal barrier layer which improves the bonding of the metal alloy coating to the metal strip. These metals have also been found to improve the corrosion-resistance of the formed intermetallic layer and inhibit the zinc intermetallic layer growth which causes problems with dross formation and impair mechanical properties, i.e. cracking due to forming. The copper is plated onto the surface of the metal strip. The plated copper layer is formed by passing the metal strip through a standard electroplating process for by adding copper sulfate to a pickling solution and pickling the copper strip. Chromium

is plated to the metal strip by a conventional plating process. Tin is coated onto the metal strip by hot dipping, plating or metal spraying.

[0072] In accordance with still another aspect of the present invention, the intermediate metal barrier layer is heated prior to the plated strip being hot dipped. The heating of the plated metal causes an intermetallic layer to begin to form and complete its formation once the strip has been hot dip coated. Such a pre-heating process results in the varying of the intermetallic layer composition which results in improved bonding and/or corrosion-resistance.

[0073] The above summary of the present invention is not intended to describe each embodiment or every implementation of the present invention. Advantages and attainments, together with a more complete understanding of the invention, will become apparent and appreciated by referring to the following detailed description and claims taken in conjunction with the accompanying drawings.

[0074] Throughout this document, all temperatures are given in degrees Celsius, and all percentages are weight percentages unless otherwise stated. All publications mentioned herein are incorporated herein by reference for the purpose of describing and disclosing the compositions and methodologies which are described in the publications which might be used in connection with the presently described invention. The publications discussed herein are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such a disclosure by virtue of prior invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0075] This invention, as defined in the claims, can be better understood with reference to the following drawings. The drawings are not necessarily to scale, emphasis instead being placed upon clearly illustrating principles of the present invention.

[0076] FIG. 1 is a zinc-aluminum binary phase diagram.

[0077] FIG. 2 depicts secondary electron images of surface of Zn23Al0.3Si alloy on steel dipped for 2 min. at 575°C; Si content of bath 0.18 wt.-%; top: 75X; bottom, 1000X.

[0078] FIG. 3 shows secondary electron image of cross sections of Zn23Al0.3Si coating; (a) thick steel sample dipped for 5 min. at 575°C in bath with 0.75 wt.-% Si; (b) thinner steel plate dipped for 5 min at 550°C in bath with 0.4 wt.-% Si.

[0079] FIG. 4 shows secondary electron images of Zn23Al0.3Si coatings on steel; (a) dipped for 1 min. in bath with 0.18 wt.-% Si at 575°C; (b) dipped for 10 min. in same bath.

[0080] FIG. 5 shows secondary electron images of Zn23Al0.3Si coatings on steel dipped for 5 min. at 575°C in bath with 0.5 wt.-% Si; (a) steel no. 2 of Table 1(low Si; low P); (b) steel no. 7 of Table 1 (high Si; low P); the Fe2Al5 layer is locally missing.

[0081] FIG. 6 shows secondary electron images of Zn23Al0.3Si coatings on steel no. 10 of Table 1 dipped for 5 min. at 575°C in bath with 0.5 wt.-% Si; (a) low magnification; (b) higher magnification; the formation of the Fe2Al5 layer is locally interrupted.

[0082] FIG. 7 shows galvanized panels after exposure in the B-117 salt spray test; (a) conventional HDG, exposed for 350 hours, showing red rust; (b) Zn23Al0.3Si-coated steel after exposure for 2000 hours; one of the panels showed one spot of red rust; the surface had darkened considerably.

[0083] FIG. 8 shows g alvanized panels after bending over 180° followed by exposure in the B-117 salt spray test; (a) conventional HDG exposed for 3 days; red rust is observed in the bent area; (b) Zn5Al-coated steel exposed for

24 days; red rust is beginning to form; (c) Zn23Al0.3Si-coated steel exposed for 24 days; no red rust is observed.

[0084] FIG. 9 shows s econdary electron images of Zn23Al0.3Si-coated steel panels after bending over 180°; (a) side of the panel that was in compression; (b) side of the panel that was in tension; this was the side viewed in Figure 8; there are no cracks in the ZnAl layer; the Fe2Al5 layer has cracked in tension.

[0085] FIG. 10 shows scribed galvanized panels before and after exposure in the B-117 salt spray test and after cleaning to remove the white rust; (a) Zn23Al03.Si-coated panels after 24 days of exposure showing protection of the scribe; (b) conventional HDG panels after 14 days showing larger amounts of white rust and formation of red rust; the scribe was still protected.

[0086] FIG. 11 depicts typical potentiodynamic polarization curve of (a) Zn23Al0.3Si-coated steel in aerated 3.5 wt.-% NaCl, showing a very active surface, absence of passivation and a corrosion potential similar to that of conventional HDG, whose curve is shown in (b).

[0087] In the following description of the illustrated embodiments, references are made to the accompanying drawings, which form a part hereof, and in which is shown by way of illustration various embodiments in which the invention may be practiced. It is to be understood that other embodiments may be utilized, and structural and functional changes may be made without departing from the scope of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0088] Before the present materials and methods for galvanizing are described, it is to be understood that this invention is not limited to the specific methodology, devices, formulations, and coatings described as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention which will be limited only by the appended claims.

[0089] One skilled in the art will readily appreciate that the present invention is well adapted to carry out the objects and obtain the ends and advantages mentioned as well as those inherent therein. It should be understood, however, that the materials, compounds, coatings, methods, procedures, and techniques described herein are presently representative of preferred embodiments. These techniques are intended to be exemplary, are given by way of illustration only, and are not intended as limitations on the scope. Other objects, features, and advantages of the present invention will be readily apparent to one skilled in the art from the following detailed description; specific examples and claims; and various changes, substitutions, other uses and modifications that may be made to the invention disclosed herein without departing from the scope and spirit of the invention or as defined by the scope of the appended claims. As would be known to one of ordinary skill in the art, many variations of nomenclature are commonly used to refer to a specific chemical composition.

[0090] In various embodiments described herein, exemplary values are specified as a range. It will be understood that herein the phrase "including all intermediate ranges and combinations thereof" associated with a given range is all integers and sub-ranges comprised within a cited range. For example, citation of a range "0.03% to 0.07%, including all intermediate ranges and combinations thereof is specific values within the sited range, such as, for example, 0.03%, 0.04%, 0.05%, 0.06%, and 0.07%, as well as

various combinations of such specific values, such as, for example, 0.03%, 0.06% and 0.07%, 0.04% and 0.06%, or 0.05% and 0.07%, as well as sub-ranges such as 0.03% to 0.05%, 0.04% to 0.07%, or 0.04% to 0.06%, etc.

[0091] Amounts of ingredients stated herein generally refer to the amount of the particular active ingredient. Amounts stated for commercial products typically relate to the amount of the commercial product. The amount of active provided by the commercial product can be determined from the concentration of the commercial product and the fraction of the commercial product that is the active ingredient.

[0092] As used herein, the term "about" modifying the quantity of an ingredient in the compositions of the invention or employed in the methods of the invention refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use compositions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients employed to make the compositions or carry out the methods; and the like. Whether or not modified by the term "about", it is intended that the claims include equivalents to the quantities.

[0093] It must be noted that as used herein and in the appended claims, the singular forms "a", "and", and "the" include plural referents unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this invention belongs. Although any methods, devices and materials similar or equivalent to those described herein can be used in the practice or testing of the invention, the preferred methods, devices and materials are now described.

[0094] By "hot dip galvanization" is meant the galvanizing of an iron or steel article by dipping in a molten bath of zinc or zinc-alloy, in continuous or batch operation.

Galvanizing with Improved Flux

[0095] The invention features devices and methods for making and using a high-aluminum alloy for general galvanizing. The present invention relates to an improvement in the fluxing step used in the galvanizing process for steel, and high aluminum-content steel made using that improved process. Such galvanizing processes, in general, are well-known and fully described in the art; they consist generally of two types: continuous galvanization and batch galvanization. See, for example, The Making, Shaping and Treating of Steel, United States Steel Corporation, 7th Edition, 1957, Pittsburgh, Chapter 39, pages 660-673, 1957, and the 10th edition, Lankford et al. (eds.), Association of Iron and Steel Engineers, Pittsburgh, 1985, pages 1173-1189, incorporated herein by reference. The improvement of the present invention is useful in any galvanizing process, but is especially useful in batch galvanization processes for steel where there is frequently a significant time delay between the fluxing of an article and the actual galvanization of that article.

[0096] In a typical batch galvanization process, the surface of the article to be galvanized is treated to remove rust and other foreign materials, the article is then fluxed and, finally, it is dipped in molten zinc to provide the galvanization. The surface preparation steps (i.e., degreasing and pickling) utilized in the process of the present invention are conventional and are known in the art. The purpose of these steps is to remove rust and other foreign materials from the surface of the steel article. This is generally accomplished by a degreasing step (to remove organic contaminants from the steel surface) in which the article is dipped in a heated alkaline solution. In a typical degreasing step, the steel article is dipped for about 5 to about 60 minutes in an alkaline solution containing sodium hydroxide and sodium orthosilicate in a weight ratio of about 1:1, and a concentration of 10 to 15%, at a temperature of about 60°C to about 80°C Other alkaline materials, such as potassium hydroxide, can be used. After this degreasing step is completed, the steel article is generally rinsed with water to remove the alkaline solution and any foreign substances (e.g., dirt and other organic particles) sticking to its surface.

[0097] This is typically followed by a pickling step (to remove mill scale and rust from the steel surface) wherein the steel article is dipped in an acid solution, preferably one containing hydrochloric acid or sulfuric acid. Pickling for sheet galvanizing is usually conducted as a batch operation in stationary tubs provided with an agitating means. This operation may sometimes be conducted as a continuous process in equipment provided with a sheet conveyor and means for electrolytic acceleration. Very light pickling, requiring only a short time exposure to the pickling solution, has been found suitable for products, such as roofing and siding, that require little mechanical deformation. Deep etching (i.e., heavy pickling) of the base metal has generally been found to be necessary when forming requirements are severe. The pickling is generally accomplished by dipping the article for as long as 5 to 30 minutes in a 10 to 15% aqueous solution of sulfuric acid (or hydrochloric acid), containing about 0.5% to about 0.7% of a pickling inhibitor, at room temperature or a temperature of about 50°C to about 70°C Higher bath temperatures require shorter immersion times. Typically, after the pickling step is concluded, the article is rinsed with water to remove excess pickling solution and iron salts sticking to the steel surface. The result of these processes is an object having a very active surface, since all the rust and other foreign materials have been removed, making it highly susceptible to oxidation.

[0098] The fluxing process of the present invention remains effective even as iron and zinc build up in the flux bath, as frequently happens as a bath is being used. Thus, the flux baths used in practicing the present invention may contain up to about 10% iron (Fe3+) and up to about 3% zinc (Zn2+).

[0099] In one embodiment, the molten zinc-aluminum alloy bath is an aluminum-zinc alloy containing at least 10, 15, 16, 17, 18, 19, 20, 21, 22, or 23% by weight of Al. In one embodiment, the molten zinc-aluminum alloy bath is an aluminum-zinc alloy containing 10%-40% by weight of Al and 0.2%-0.7% by weight of Si and the remainder is zinc. In one embodiment, the molten zinc-aluminum alloy bath is an aluminum-zinc alloy containing 20%-25% by weight of Al and 0.2%-0.5% by weight of Si and the remainder is zinc.

[00100] In a further embodiment, the aluminum accounts for about 10 to about 40 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the aluminum accounts for about 20 to about 25 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the aluminum accounts for about 22 to about 24 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the aluminum accounts for about 23 wt % of the molten zinc-aluminum alloy bath.

[00101] In a further embodiment, the silicon accounts for about 0.18 to about 0.75 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the silicon accounts for about 0.2 to about 0.7 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the silicon accounts for about 0.3 to about 0.5 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the silicon accounts for about 0.3 wt % of the molten zinc-aluminum alloy bath.

[00102] In another embodiment, the galvanizing step is carried out for from about 1 to about 5 minutes at a temperature of from about 500°C to about 600°C. In another embodiment, the galvanizing step is carried out for from about 2 minutes to about 3 minutes at a temperature of from about 510°C to about 530°C. In another embodiment, prior to coating, the article is degreased by dipping it in an alkaline solution and is pickled by dipping it in an acid solution.

[00103] The temperature of the molten zinc-aluminum alloy bath in a separate dip galvanizing vessel is generally from about 400 to about 650°C. In one embodiment, the temperature of the molten zinc-aluminum alloy bath is from about 500 to about 650°C. In another embodiment, the temperature of the molten zinc-aluminum alloy bath is from about 500 to about 625°C. In another embodiment, the temperature of the molten zinc-aluminum alloy bath is from about 550 to about 625°C.

[00104] The mechanics of the galvanizing step are well-known in the art. In this step, for example, the fluxed article is dipped into a molten zinc bath for about three minutes at a temperature of about 510-530°C Typically, the residence time in the bath is from about 1 to about 5 minutes, preferably from about 2 to about 3 minutes, most preferably about 3 minutes, and the bath temperature is from about 500°C to about 600°C, preferably from

about 510°C to about 530°C The precise residence time and temperature can be adjusted based on the content of the galvanization bath, the steel to be coated, and the characteristics desired, to optimize the process. The equipment typically used for sheet galvanizing consists of mechanical facilities for transporting cut length sheets or other articles successively through acid washing, fluxing, hot-dipping, and cooling operations. The coating bath, itself, is contained in a heated low carbon steel vessel or pot. A framework or rigging, typically including suitable entry feed rolls, sheet guides, driven bottom pinch rolls, and driven exit rolls, is suspended in the bath in such a manner as to completely submerge all but the entry rolls, part of the exit rolls, and part of the supporting framework.

[00105] Small quantities of other metals may be added to the zinc-aluminum bath to control the appearance and properties of the coatings formed. For example, lead, antimony, nickel, magnesium, manganese, tin, bismuth, cobalt, or mixtures of these metals may be added at low concentrations to control viscosity of the bath (which, in turn, controls thickness of the coating), dross formation and reactivity of the bath, as well as other coating properties.

[00106] In one embodiment the present invention is the inclusion of aluminum in the zinc-galvanizing bath. Conventional fluxing processes are incompatible with the use of aluminum in the galvanizing step, since those fluxing processes result in a zinc ammonium chloride layer being formed on the fluxed steel, the chloride layer reacting negatively with aluminum in the galvanizing bath. The flux described herein, however permits the inclusion of relatively high levels of aluminum in the zinc galvanization bath. In fact, the galvanization bath herein comprises from about 17% to about 40 wt.% preferably from about 20% to about 30 wt.% most preferably about 23 wt.% (the zinc-aluminum eutectoid composition) by weight aluminum, together with from about 0.18% to about 0.75 wt.% silicon, preferably from about 0.2% to about 0.7% silicon, more preferably from about 0.2% to about 0.5 wt.% silicon, most preferably about 0.3 wt.% silicon and from about 60% to about 83%, preferably from about 70% to about 80% zinc, most preferably about 78% zinc. By "hot dip galvanization" is meant the galvanizing of an iron or steel article by

dipping in a molten bath of zinc or zinc-alloy, in continuous or batch operation.

[00107] A flux for hot dip galvanization in accordance with the invention comprises: 60 to 80 wt. % (percent by weight) of zinc chloride ($ZnCl_2$); 7 to 20 wt. % of ammonium chloride (NH_4Cl). In one embodiment, the flux further comprises 2 to 20 wt. % of at least one alkali or alkaline earth metal salt. In one embodiment, the flux further comprises 0.1 to 5 wt. % of a least one of the following compounds: NiCl2, CoCl2, MnCl2. In one embodiment, the flux further comprises 0.1 to 1.5 wt. % of at least one of the following compounds: PbCl2, SnCl2, SbCl3, BiCl3.

[00108] Such a flux, wherein the different percentages relate to the proportion in weight of each compound or compound class relative to the total weight of the flux, makes it possible to produce continuous, more uniform, smoother and void-free coatings on iron or steel articles by hot dip galvanization with zinc-aluminum alloys, especially in batch operation. The selected proportion of $ZnCl_2$ ensures a good covering of the article to be galvanized and effectively prevents oxidation of the article during drying of the article, prior to the galvanization. The following compounds: NiCl2, CoCl2, MnCl2, are believed to further improve by a synergistic effect the wettability of steel by molten metal. The presence in the flux of between 0.1 to 1.5 wt. % of at least one of PbCl2, SnCl2, BiCl3 and SbCl3 permits to improve the wetting of an iron or steel article, covered with this flux, by molten zinc in a galvanizing bath. As mentioned, the present flux is particularly suitable for batch hot dip galvanizing processes using zinc-aluminum alloys but also pure zinc. Moreover, the present flux can be used in continuous galvanizing processes using either zinc-aluminum or pure zinc baths, for galvanizing e.g. wires, pipes or coils (sheets) . . . The term "pure zinc" is used herein in opposition to zinc-aluminum alloys and it is clear that pure zinc galvanizing baths may contain some additives such as e.g. Pb, Sb, Bi, Ni, Sn.

[00109] In one embodiment, the proportion of zinc chloride is between 70 and 78% by weight relative to the total weight of the flux. In another embodiment, a proportion of 11 to 15% by weight of ammonium chloride is used. The

NiCl2 content in the flux is preferably of 1% by weight. In another embodiment, the flux comprises up to 1% by weight of PbCl2.

[00110] Referring more specifically to the alkali or alkaline earth metals, they are advantageously chosen from the group (sorted in decreasing order of preference) consisting of: Na, K, Li, Rb, Cs, Be, Mg, Ca, Sr, Ba. The flux shall advantageously comprise a mixture of these alkali or alkaline earth metals, as they have a synergistic effect which allows to control the melting point and the viscosity of the molten salts and hence the wettability of the surface of the article by the molten zinc or zinc-aluminum alloy. They are also believed to impart a greater thermal resistance to the flux. In another embodiment, the flux comprises up to about 6% by weight of NaCl and 2% by weight of KCl.

[00111] According to another aspect of the invention, a fluxing bath for hot dip galvanization is proposed, in which a certain amount of the above defined flux is dissolved in water. The concentration of the flux in the fluxing bath may be between 200 and 700 g/l. In one embodiment, the concentration of the flux in the fluxing bath is between 350 and 550 g/l. In another embodiment, the concentration of the flux in the fluxing bath is between 500 and 550 g/l. This fluxing bath is particularly adapted for hot dip galvanizing processes using zinc-aluminum baths, but can also be used with pure zinc galvanizing baths, either in batch or continuous operation.

[00112] In one embodiment, the fluxing bath is maintained at a temperature between 30 and 90°C. In one embodiment, the fluxing bath is maintained at a temperature between 40 and 80°C. In one embodiment, the fluxing bath is maintained at a temperature of at least 70°C

[00113] The fluxing bath may also comprise 0.01 to 2 vol. % (by volume) of a non-ionic surfactant, such as e.g. Merpol HCS from Du Pont de Nemours, FX 701 from Henkel, Netzmittel B from Lutter Galvanotechnik Gmbh or the like.

[00114] In one embodiment, to set the desired ratio of zinc chloride to alkali metal chloride of the flux salt mixture on the material being galvanized, the flux salt composition according to the invention contains about 10 to about 80% by weight. In another embodiment, the flux salt composition

according to the invention contains about 25 to about 70% by weight. In another embodiment, the flux salt composition according to the invention contains about 50 to about 70% by weight of zinc chloride, based on the salt content of the flux salt.

[00115] In one embodiment, the flux salt composition contains from about 20 to about 90% by weight. In one embodiment, the flux salt composition contains from about 30 to about 75% by weight. In one embodiment, the flux salt composition contains from about 30 to 50% by weight of alkali metal chloride, based on the salt content of the flux salt.

[00116] In one embodiment, the flux additionally comprises zinc oxide or alkali metal hydroxides, in particular lithium hydroxide, sodium hydroxide and/or potassium hydroxide, metal carbonates, zinc carbonate, or a combination thereof.

[00117] In one embodiment, the flux additionally comprises from about 1 to about 20% by weight. In one embodiment, the flux additionally comprises from about 2 to about 10% by weight. In one embodiment, the flux additionally comprises from about 3 to about 7% by weight, of zinc oxide, based on the flux salt.

[00118] Alkali metal permanganate, especially potassium permanganate, is advantageous as an oxidizing constituent, since it can oxidize both iron and organic contaminants, and manganese(II) which forms can be removed again as manganese dioxide using methods which are known per se, but it is also possible to use metal peroxides and/or metal chlorates, such as zinc peroxide or zinc chlorate, as oxidizing constituents.

[00119] The quantity of permanganate included ideally results from the stoichiometric demand for oxidation of all the included iron(II) to form iron(III). Consequently, in one embodiment, the flux comprises a content of from about 0.1 to about 15% by weight. In another embodiment, the flux comprises a content of from about 0.5 to about 10% by weight. In yet another embodiment, the flux comprises a content of from about 1 to about 5% by weight, of alkali metal permanganate, based on the flux salt in the flux salt composition. In one embodiment, the alkali metal permanganate is potassium permanganate.

[00120] A further embodiment of the present invention relates to a fluxing agent solution which is used to treat iron-containing metal surfaces prior to the galvanization and contains a flux salt of the above composition. In one embodiment, this fluxing agent solution is to have a concentration of less than about 40 g/l. In one embodiment, this fluxing agent solution is to have a concentration of less than about 30 g/l. In another embodiment, this fluxing agent solution is to have a concentration of less than about 25 g/l of iron.

Galvanizing with Molten Flux

[00121] In one embodiment, the present invention provides a method of galvanizing with a molten zinc-aluminum alloy as described above by immersing an oxide-film free steel material in a molten flux bath in an independent vessel and thereafter immersing the flux coated steel material in a molten zinc-aluminum alloy bath in a separate vessel to be coated with a zinc-aluminum alloy layer.

[00122] In one embodiment, the molten flux bath consists essentially of at least one metal chloride selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides, and the balance being zinc chloride.

[00123] In one embodiment, the at least one metal chloride selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides is sodium chloride and accounts for 5-25 wt %, preferably 5-22 wt %, and most preferably 10-20 wt % of the molten flux bath.

[00124] In one embodiment, the molten flux bath consists essentially of at least one metal chloride selected from the group consisting of alkali metal chlorides, alkaline earth metal chlorides, an alkali metal fluoride, and the balance being zinc chloride.

[00125] In one embodiment, the at least one metal chloride selected from the group consisting of alkali metal chlorides and alkaline earth metal chlorides is sodium chloride and accounts for 5-25 wt %, preferably 5-22 wt %, and most preferably 10-20 wt % of the molten flux bath; and said alkali metal

fluoride is sodium fluoride and accounts for 1-5 wt % of the molten flux bath.

[00126] In one embodiment, the molten flux bath is held at 400-560° C.

[00127] An iron or steel material that has been freed of the surface oxide film by preliminary treatments is immersed in a molten flux bath in an independent vessel, whereupon the material to be galvanized is made sufficiently clean by the cleaning action of the molten high temperature zinc chloride in the flux, so that the withdrawn material, although it has a zinc chloride layer deposited thereon, can be immediately immersed in a molten zinc alloy bath in a separate vessel, whereupon an alloy coating readily forms on the material. Thereafter, the material may be withdrawn as such to yield an article having a smooth and beautiful coating of a zinc-aluminum alloy on the surface.

[00128] In one embodiment, the molten flux bath and the molten zinc alloy bath are held in separate vessels, so the temperatures of the two baths can be controlled independently of each other. In one embodiment, the temperature of the molten flux bath in an independent vessel must be higher than the melting point of the flux composition. In one embodiment, the range of the temperature of the molten flux bath is between 300 and 500° C. In another embodiment, the range of the temperature of the molten flux bath is between 300 and 400° C. In one embodiment, the range of the temperature of the molten flux bath is between 400 and 560° C.

[00129] In one embodiment, the temperature of the molten zinc-aluminum alloy bath in a separate dip galvanizing vessel depends on the aluminum content of the alloy.

[00130] In one embodiment, the molten zinc-aluminum alloy bath is an aluminum-zinc alloy containing at least 10, 15, 16, 17, 18, 19, 20, 21, 22, or 23% by weight of Al. In one embodiment, the molten zinc-aluminum alloy bath is an aluminum-zinc alloy containing 10%-40% by weight of Al and 0.2%-0.7% by weight of Si and the remainder is zinc. In one embodiment, the molten zinc-aluminum alloy bath is an

aluminum-zinc alloy containing 20%-25% by weight of Al and 0.2%-0.5% by weight of Si and the remainder is zinc.

[00131] In a further embodiment, the aluminum accounts for about 10 to about 40 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the aluminum accounts for about 20 to about 25 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the aluminum accounts for about 22 to about 24 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the aluminum accounts for about 23 wt % of the molten zinc-aluminum alloy bath.

[00132] In a further embodiment, the silicon accounts for about 0.18 to about 0.75 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the silicon accounts for about 0.2 to about 0.7 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the silicon accounts for about 0.3 to about 0.5 wt % of the molten zinc-aluminum alloy bath. In another embodiment, the silicon accounts for about 0.3 wt % of the molten zinc-aluminum alloy bath.

[00133] In a further embodiment, the metal layer has a thickness of from about 1 nm to about 10 μm. In a further embodiment, the fluxing step is carried out for from about 1 to about 10 minutes, at a temperature of from about room temperature to about 100°C. In another embodiment, the fluxing step is carried out at a temperature of from about 20°C to about 50°C. In another embodiment, the fluxing step is carried out at a temperature of from about 22°C to about 35°C. In another embodiment, the metal is selected from the group consisting of low carbon steels, ultra-low carbon steels, titanium steels, chromium steels and stainless steels.

[00134] In another embodiment, the galvanizing step is carried out for from about 1 to about 5 minutes at a temperature of from about 500°C to about 600°C. In another embodiment, the galvanizing step is carried out for from about 2 minutes to about 3 minutes at a temperature of from about 510°C to about 530°C. In another embodiment, prior to fluxing, the article is degreased by dipping it in an alkaline solution and is pickled by dipping it in an acid solution.

[00135] In the present invention, the molten flux bath and the molten zinc alloy bath are held in separate vessels, so the temperatures of the two baths can be controlled independently of each other. The temperature of the molten flux bath in an independent vessel must be higher than the melting point of the flux composition. In one embodiment, the range of the temperature of the molten flux bath is between 400 and 600°C. In another embodiment, the range of the temperature of the molten flux bath is between 500 and 600°C. In another embodiment, the range of the temperature of the molten flux bath is between 510 and 600°C. In another embodiment, the range of the temperature of the molten flux bath is between 510 and 550°C.

[00136] The temperature of the molten zinc-aluminum alloy bath in a separate dip galvanizing vessel is generally from about 400 to about 650°C. In one embodiment, the temperature of the molten zinc-aluminum alloy bath is from about 500 to about 650°C. In another embodiment, the temperature of the molten zinc-aluminum alloy bath is from about 500 to about 625°C. In another embodiment, the temperature of the molten zinc-aluminum alloy bath is from about 550 to about 625°C.

[00137] Compared to a zinc bath, the surface of the zinc-aluminum alloy bath undergoes less oxidation with air and is covered with a only thin oxide film. As already mentioned, in the case of galvanizing by a conventional wet method (hot dipping process) in which a blanket molten flux layer floats on a zinc bath, the galvanized material is passed through the molten flux layer to be withdrawn from the zinc bath and, hence, suffers from the disadvantage that the flux easily deposits on the surface of the galvanized layer. In one embodiment, the galvanized material is simply withdrawn after the removal by skimming of the thin oxide film on the surface of the galvanizing bath and, a galvanized layer having a clean and smooth surface without any flux deposits can be easily obtained.

[00138] In one embodiment, the flux composition may consist solely of zinc chloride. However, due to extensive evaporation of zinc chloride, the working environment is contaminated to cause various problems such as the clogging of the bag of a dust collector. To deal with this difficulty, the flux composition is typically adjusted to consist essentially of 5-25 wt %,

preferably 5-22 wt % and most preferably 10-20 wt %, of a chloride of an alkali metal such as sodium, potassium or lithium or a chloride of an alkaline earth metal such as calcium or magnesium, 1-7 wt %, preferably 1-5 wt %, of a fluoride of an alkali metal such as sodium, potassium or lithium and the balance being zinc chloride. Chlorides of alkali metals are typified by sodium chloride, and fluorides of alkali metals are typified by sodium fluoride. When in a high temperature molten state, particularly at a temperature in the range of 400-560° C., zinc chloride has an outstanding cleaning effect on the surfaces of iron or steel materials. The addition of chlorides of alkali metals or alkaline earth metals not only lowers the melting point of the flux, but also proves surprisingly effective in suppressing the evaporation of zinc chloride; they also have a cleaning effect and a flux fluidizing action, as well as serve to be a partial substitute for the zinc chloride as an extender. Fluorides of alkali metals also have a cleaning effect and a flux fluidizing action; in addition, they are effective in enhancing the gloss of the galvanized surface.

[00139] If the chlorides of alkali metals or alkaline earth metals are added in amounts less than 5 wt %, they are not highly effective in suppressing the evaporation of zinc chloride; if their addition exceeds 25 wt %, the melting point of the flux increases to increase the chance of its deposition on the iron or steel materials and the occurrence of black spottings (ungalvanized areas). If the alkali metal fluorides are also added in preferred amounts of 1-5 wt %, more preferably about 3wt %, the gloss of the galvanized surface can be improved. No significant improvement in the gloss can be achieved if less than 1 wt % of the alkali metal fluorides is added; if they are added in more than 7 wt %, black spottings (ungalvanized areas) are prone to occur. Needless to say, it is within the scope of the invention to use two or more alkali metal or alkaline earth metal chlorides in combination in the flux.

[00140] Examples of the steel material to be galvanized by the galvanizing method of the invention include low carbon steels, ultra-low carbon steels, titanium steels, chromium steels and stainless steels. The galvanizing method of the invention is applicable not only to steel structures or related components thereof, but also to sheets and wires; therefore, the

applicability of the invention method covers both batchwise and continuous operations,

Galvanizing without Flux

[00141] There are several applications of the new alloy where a flux treatment is not required. These are in the continuous galvanizing of sheets, tubes and wires. In the first two applications, coatings of pure zinc are typically applied. In continuous wire galvanizing, the alloy Galfan® (Zn5Al) is often used. The coating thickness can be lower than in the batch galvanizing processes, e.g., 5-10 μm versus 75-100 μm. Therefore, there is a need for more corrosion resistant alloys in these applications without losing mechanical properties such as ductility.

[00142] In one embodiment, the steel surface is prepared for the galvanizing process by first pickling the steel in an acid. The oxide is largely removed in this step. In one embodiment, the sheet, tube or wire runs through a furnace with a reducing atmosphere.

[00143] The reducing atmosphere is not critical as long as it is a reducing atmosphere. In one embodiment, N_2 gas containing at least 0.5% of H_2 or H_2 gas is used. In one embodiment, N_2 gas containing 1 to 20%, typically about 5% of H_2 is used.

[00144] In one embodiment, the wire, sheet or tube is heated to near the temperature of the zinc bath while at the same time all the oxides are removed by reactions with the reducing gas. In one embodiment, the wire, sheet or tube is heated to within 200°C of the temperature of the zinc bath. In one embodiment, the wire, sheet or tube is heated to within 100°C of the temperature of the zinc bath. In one embodiment, the wire, sheet or tube is heated to within 75°C of the temperature of the zinc bath. In one embodiment, the wire, sheet or tube is heated to within 50°C of the temperature of the zinc bath. In one embodiment, the wire, sheet or tube is heated to within 25°C of the temperature of the zinc bath.

[00145] Due to the cleanliness of the steel when it is immersed in the liquid zinc (alloy) bath, the wettability of the steel by the liquid metal is very good. The residence time in the bath can, therefore, be as short as a few seconds.

Again, due to the cleanliness of the steel substrate, the adhesion of the zinc (alloy) layer is also good.

[00146] Obviously, in this process only a so-called drag-out layer of the zinc (alloy) is formed on the steel article. This layer has exactly the composition of the liquid metal. In other word, there is almost no time for the formation of iron-zinc or iron-aluminum alloys at the interface with the steel. Thus, the corrosion resistance of galvanized products so obtained is considerably less that that of batch galvanized products, which have a much thicker coating layer and which also form intermetallic alloy layers.

[00147] Nevertheless, the Zn23Al0.3Si alloy system described above performs much better than the currently used zinc or Zn5Al (Galfan®) system in humidity and salt spray exposure tests. The rate of white rust formation is considerably lower and the rate of zinc leaching into the environment is also lower than that of conventional products.

[00148] In one embodiment, during the process of coating Zn23Al0.3Si alloy on sheets, wires or tubes, it will be possible to stimulate the formation of interfacial iron-aluminum alloys to a certain extent, by lowering the silicon content as compared with the batch process.

[00149] The present invention is applicable to the plating of a metal tubing or wire including a steel, copper, tungsten and other metal wires and tubes. A typical chemical composition of a steel wire or tube used for the purpose of the present invention is, in mass, 0.02 to 1.15% of C, 1% or less of Si and 1% or less of Mn, i.e. a chemical composition of a commonly used steel wire or tube. A steel containing, in mass, 0.02 to 0.25% of C, 1% or less of Si and 0.6% or less of Mn is used especially for a metal wire for forming nets.

[00150] Corrosion resistance of a hot dip galvanized steel wire or tubing or a hot dip zinc alloy plated steel wire or tubing obtained according to the present invention may be further enhanced by coating one or more of the high molecular compounds selected from among vinyl chloride, polyethylene, polyurethane and fluororesin. In this case, adhesion is enhanced by an anchoring effect caused by the high molecular compounds firmly penetrating the rough surface and the plated tubing or wire has the effect

of being durable to the drawing in the longitudinal direction of the tubing or wire.

Galvanizing Pretreatments

[00151] In one embodiment, the process mainly comprises the steps of pretreating an iron or steel article to be coated, treating it with the flux, coating it in a galvanizing bath containing a molten zinc-aluminum alloy and cooling it. In another embodiment, the process mainly comprises the steps of pretreating an iron or steel article to be coated, treating it with a molten flux, coating it in a galvanizing bath containing a molten zinc-aluminum alloy and cooling it. In another embodiment, the process mainly comprises the steps of pretreating an iron or steel article to be coated, heating it in a reducing atmosphere, coating it in a galvanizing bath containing a molten zinc-aluminum alloy and cooling it.

[00152] In one embodiment, an oxide layer adhered on a surface of a steel material is removed by pickling with an acid such as an aqueous hydrochloric acid or sulfuric acid solution and then rinsing with water (hereinafter, water rinsing) and an activating treatment are conducted. In one embodiment, an oxide layer is removed by mechanical means such as shot blast, grit blast, etc., and then brief acid pickling treatment is conducted and water rinsing treatment, or only water rinsing and activating treatment are conducted.

[00153] In one embodiment, this process is applicable for a large variety of steel articles, such as e.g. large structural steel parts as for towers, bridges and industrial or agricultural buildings, pipes of different shapes as for fences along railways, steel parts of vehicle underbodies (suspension arms, engine mounts . . .), castings and small parts.

[00154] In one embodiment, the pretreatment of the article is firstly carried out by dipping the article to be galvanize in an alkali degreasing bath comprising: a salt mix including mainly sodium hydroxide, sodium carbonate, sodium polyphosphate as well as a tenside mix, such as e.g. Solvopol SOP and Emulgator SEP from Lutter Galvanotechnik GmbH. In one embodiment, the concentration of the salt mix is between 2 and 8 wt. % and that of the tenside mix is between 0.1 and 5 wt. %. In one embodiment, the degreasing bath is kept at a temperature of 60° C. to 80° C. In one

embodiment, an ultrasonic generator is provided in the bath to assist the degreasing. In one embodiment, this step is followed by one or more water rinsings.

[00155] In one embodiment, the pretreatment then continues with a pickling step, wherein the article is dipped in an aqueous solution of hydrochloric acid containing an inhibitor (hexamethylene tetramine, . . .) to remove scale and rust from the article. In one embodiment, the pretreatment then continues with a pickling step, wherein the article is dipped for 60 to 180 minutes in a 10 to 22% aqueous solution of hydrochloric acid containing an inhibitor (hexamethylene tetramine, . . .) and kept at a temperature of 30 to 40° C. to remove scale and rust from the article. In one embodiment, this is followed by one or more rinsing steps. In one embodiment, rinsing after pickling is carried out by dipping the article in a water tank at a pH lower than 1 for less than 3 minutes, more preferably for about 30 seconds. It is clear that these steps of degreasing and pickling can be repeated if necessary.

[00156] In one embodiment, the fluxing treatment is carried out in a fluxing bath, in which the above described flux is dissolved in water. In one embodiment, the fluxing bath, in which the flux concentration preferably is between 350 and 550 gA, is maintained at a temperature of about 70° C. and its pH should be between 1.5 and 4.5. In one embodiment, the article is dipped in the fluxing bath for not more than 10 minutes, preferably for about 3 to 5 minutes, whereby a layer of wet flux is formed on the article's surface.

[00157] In one embodiment, the article is then dried in a forced air stream having a temperature of about 250° C. In one embodiment, the article is preferably dried until its surface exhibits a temperature of between 170 and 200° C. It is however clear that this preheating of the article, i.e. imparting a certain amount of heat to the article before the galvanizing, does not need to be carried out during the drying step following the fluxing. In one embodiment, it can be performed in a separate preheating step, directly after the drying or, in case the article is not to be immediately galvanized, at a later stage.

[00158] In one embodiment, thee galvanizing bath advantageously contains (in weight): 4.2-7.2% of Al, 0.005-0.15% of Sb and/or 0.005 to 0.15% of Bi, max. 50 ppm of Pb, max. 50 ppm of Cd, max. 20 ppm of Sn, 0.03-0.10% of mischmetals, max. 150 ppm of Si, max. 750 ppm of Fe, and the remainder of Zn. This galvanizing bath is maintained at a temperature of 380 to 700° C.

[00159] In one embodiment, the fluxed and preferably preheated article is dipped for about 1 to 10 minutes in the galvanizing bath. It is clear that the dipping time mainly depends on the overall size and shape of the article and the desired coating thickness. During the first minutes of the dipping, the article is preferably moved in the bath so as to assist the remelting of the frozen metal layer that forms on the article surface. In addition, bubbling is advantageously carried out in the bath by means of N_2 introduced into the galvanizing bath in the form of fines bubbles. This can be achieved by providing e.g. a gas diffuser made of ceramic or sintered stainless steel, in the galvanizing bath. After the passage of an appropriate dipping time, the coated article is lifted from the bath at an appropriate speed, so that the liquid alloy may be removed from it, leaving a smooth, ripple-free, continuous coating on the article's surface.

[00160] In one embodiment, the cooling of the coated article is carried out by dipping it in water having a temperature of 30° C. to 50° C. or alternatively, by exposing it to air. As a result, a continuous, uniform and smooth coating free from any voids, bare spots, roughness or lumpiness, is formed on the article's surface.

Additional Embodiments

[00161] In one embodiment, the metal strip is pre-treated prior to applying the metal alloy coating. In one embodiment, the pretreatment process includes several steps for metals such as stainless steel or includes only a few steps for metals which are easier to clean and/or have a pre-activated surface when received in coil form. Commercial stainless steel usually has a passivated surface which is difficult to consistently and uniformly coat in a high speed hot-dipped process. "High speed" means a residence time in a molten bath of less than 1.0 minute and less than 30 seconds. The

pretreatment process is preferably similar to the process disclosed in Assignees' U.S. patent application Ser. No. 000,101 and incorporated herein. The pretreatment process typically includes pickling and chemical activation of the metal strip surface.

[00162] The pickling process is formulated to remove a very thin surface layer from the metal strip surface. The removal of a very thin layer from the surface of the metal strip results in the removal of oxides and other foreign matter from the metal strip surface thereby activating the surface prior to applying the metal alloy coating. When coating stainless steel, it is especially important to activate the stainless steel surface in order to form a strong bonding and uniformly coated metal alloy coating. Stainless steel contains chromium and iron. The chromium in the stainless steel surface reacts with atmospheric oxygen to form chromium oxide. The chromium oxide film creates an almost impenetrable barrier to protect the iron within the stainless steel from the oxygen in the atmosphere, thus inhibiting the oxygen to combine with the iron to form iron oxides. The chromium oxide film also forms a very tight and strong bond with the stainless steel and is not easily removed. Although the formation of the chromium oxide film is important in the corrosion-resistant properties of the stainless steel and is intended for commercial stainless steel, the chromium oxide film of commercial stainless steel interferes with the bonding of a thin layer of hot-dipped metal alloy coating to the stainless steel surface resulting in weak metal alloy coating bonding and in flaking. The surface activation of a stainless steel strip, as with other metal strip, is accomplished by removing the oxides on the surface of the metal strip. The removal of a chromium oxide film from the stainless steel surface activates the stainless steel strip surface. Testing of stainless steel strip has revealed that the removal of chromium oxide film improves the bonding of the metal alloy coating and allows for thick and/or uniform metal alloy coatings to be formed. Oxide removal on other metal strip also improves the bonding and coating thickness of the metal alloy coating. The pickling process removes the detrimental oxide layer to facilitate in the formation of a strong bonding and uniform metal alloy coating.

[00163] The pickling process slightly etches the metal strip surface to remove a very thin layer of the surface. The rate of etching is usually not the same throughout the surface of the metal strip thereby forming microscopic valleys on the metal strip surface which increases the surface area for which the metal alloy coating bonds to the metal strip.

[00164] The pickling process includes the use of a pickling solution which removes and/or loosens the oxide from the metal strip surface. The pickling solution contains various acids or combinations of acids such as hydrofluoric acid, sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid and/or isobromic acid. Hydrochloric acid solutions are preferably used to pickle carbon steel. A specially formulated pickling solution should be used when the metal strip is stainless steel since the activation of a stainless steel surface is not properly accomplished by use of prior art pickling solutions containing only sulfuric acid, nitric acid or hydrochloric acid. The specially formulated pickling solution contains a special combination of hydrochloric acid and nitric acid. This special dual acid formulation was found to be surprisingly effective in the rapid removal of chromium oxide from stainless steel substrates. The use of this dual acid solution is classified as aggressive pickling of the metal strip. The dual acid composition of the pickling solution preferably includes 5-25% hydrochloric acid and 1-15% nitric acid and preferably about 10% hydrochloric acid and 3% nitric acid. The dual acid results in limited etching of the stainless steel to increase the surface area without causing detrimental pitting of the stainless steel surface. The control of the temperature of the pickling solution is important so as to provide a desired activity of the acid to remove the oxides from the metal surface. The temperature of the pickling solution is maintained above 80° F. and usually between 120°-140° F. and preferably 128°-133° F. Higher acid concentration and/or higher temperatures will increase the activity and aggressiveness of the pickling solution in the removal of oxides. The temperature of the pickling solution is preferably maintained by recirculation through heat exchangers.

[00165] The pickling solution is preferably agitated to prevent the solution from stagnating, varying in concentration, varying in temperature, and/or to

remove gas pockets which form on the metal strip surface. Agitation of the pickling solution is carried out by placing agitators in the pickling tank and/or recirculating the pickling solution. Agitation brushes preferably are placed within the pickling tank to agitate the acid solution and scrub the metal surface immersed in the acid solution. The metal strip is preferably scrubbed during the aggressive pickling process to facilitate in the activation of the metal strip surface. Scrubbing the metal surface increases and accelerates the removal of oxides from the metal surface.

[00166] Only one pickling tank is needed to properly activate the metal strip surface; however, additional pickling tanks can be used. The pickling tanks are about twenty-five feet in length; however, the size of the tank may be longer or shorter. The total time for pickling the metal strip is preferably less than 10 minutes, more preferably less than a minute and even more preferably about 10 to 20 seconds to properly activate the metal strip. The metal strip is preferably processed in a continuous process, the pickling tanks are usually 25 feet in length and the sheet strip is run through the pickling tanks at a rate of 1-400 ft/min, preferably between 50 to 250 ft/min thereby subjecting the metal strip to the pickling solution in each pickling tank for preferably less than one minute. The sheet strip is preferably unrolled from a roll of metal strip and guided through the continuous process, i.e. unroll the metal strip, process and coat the strip, and roll up the coated strip.

[00167] Once the metal strip has been pickled, the metal strip is preferably treated in a chemical activation process. The chemical activation process further removes oxides and foreign material from the metal strip by subjecting the metal strip surface to a deoxidizing agent. After the pickling process, very little oxide, if any, is present on the metal surface. The virgin surface is highly susceptible to forming oxides between the time period the metal strip is removed from the pickling tank and being coated by a hot-dip process. When the metal strip is sufficiently activated by only the pickling process, the chemical activation step is eliminated. Due to the difficulty in removing oxides from stainless steel strip, a stainless steel strip is preferably treated in the chemical activation process after the stainless steel strip has been treated in the pickling process. Various types of

deoxidizing solutions have been tested. Zinc chloride has been found to be an excellent deoxidizing solution. In one embodiment, the zinc chloride acts as both a deoxidizer and a protective coating from oxide formation for the metal strip surface. In one embodiment, the temperature of the zinc chloride solution is kept at about ambient temperature (60°-90° F.) and is agitated to maintain a uniform solution concentration and temperature. Small amounts of hydrochloric acid are preferably added to the deoxidizing solution to further enhance oxide removal. In one embodiment, the hydrochloric acid is added to the zinc chloride when treating a stainless steel strip. The time the metal strip is subjected to the deoxidizing solution is usually less than 10 minutes. In one embodiment, the metal strip is processed in a continuous process. In one embodiment, the deoxidization solution tanks are 25 feet in length and the metal strip is subjected to the deoxidation solution for less than one minute.

[00168] In one embodiment, the strip is treated with an abrasive and/or absorbent material and/or subjected to a solvent or other type of cleaning solution to remove foreign materials and oxides from the metal strip surface prior to pickling and/or chemical activation of the strip. Metal strip that is unrolled from a roll of metal strip commonly has foreign debris on the surface of the metal strip. Such debris may consist of dirt, oil, glue, etc. Many of these foreign substances do not react with or are not readily removable by the pickling solution, thus adversely affecting the removal of oxides from the metal strip. Treating the metal strip with an abrasive and/or absorbent material removes these foreign substances from the metal strip. The brushes are stationary or moving relative to the metal strip. The brushes roughen the surface of the metal strip to further enhance the activation of the metal strip during the pickling process. The roughed up surface of the metal strip allows the pickling solution to more readily attack the surface of the metal strip.

[00169] In one embodiment, the pretreatment process preferably includes the maintaining of a low oxygen environment prior to and/or subsequent to subjecting the metal strip to the pickling process and/or chemical activation process and/or abrasion process. The maintenance of a low oxygen environment inhibits the formation and/or reformation of oxides

on the metal strip surface. In one embodiment, the low oxygen environment may take on several forms. Two examples of low oxygen environments are the formation of a low oxygen-containing gas environment about the metal strip or the immersion of the metal strip in a low oxygen-containing liquid environment. Both these environments act as shields against atmospheric oxygen and prevent and/or inhibit oxides from forming. When the metal strip is stainless steel, the low oxygen environment is preferably maintained throughout the pretreatment process of the stainless steel strip (i.e. abrasive/absorbent treatment, pickling treatment, pickling rinse treatment, chemical activation treatment, etc.) to just prior to the coating of the stainless steel strip with the metal alloy coating. Metals other than stainless steel can be totally, partially, or not subjected to a low oxygen environment during the pretreatment process. The non-oxidized surface of a metal strip is highly susceptible to re-oxidation when in contact with oxygen. By creating a low oxygen environment about the metal strip, new oxide formation is inhibited and/or prevented.

[00170] Examples of low oxygen gas environments include nitrogen, hydrocarbons, hydrogen, noble gasses and/or other non-oxidizing gasses. Preferably, nitrogen gas is used to form the low oxygen gas environment. Examples of low oxygen liquid environment include non-oxidizing liquids and/or liquids containing a low dissolved oxygen content. An example of the latter is heated water sprayed on the surfaces of the metal strip; however, the metal strip is alternatively immersed in heated water. Heated water contains very low levels of dissolved oxygen and acts as a shield against oxygen from forming oxides with the metal strip. The spray action of the heated water removes any remaining pickling solution or deoxidizing solution from the metal strip. The temperature of the heated water is maintained above about 100° F. and preferably at least about 110° F. or greater so as to exclude the unwanted dissolved oxygen.

[00171] In accordance with still yet another aspect of the present invention, the metal strip is rinsed with liquid after exiting the pickling solution to remove the pickling solution from the metal strip. After the metal strip exits the pickling solution, any pickling solution remaining on the metal

strip continues to eat into the surface of metal strip thereby resulting in pitting of the metal strip. The pickling solution is preferably removed from the metal strip by passing the metal strip through a body of water. The water is above 80° F. and preferably be at least about 110° F. so as to exclude the dissolved oxygen from the water to prevent oxidation of the post-pickled metal strip. The rinse solution is preferably maintained at its desired temperature by recirculating the rinse solution through heat exchangers. Although the rinse process primarily removes the pickling solution from the metal strip, the rinse process also removes loosened oxides from the metal strip surface. The rinse solution removes small amounts of oxides due to the slightly acidic nature of the rinse solution. As the rinse solution removes the pickling solution from the metal strip, the pickling solution enters the rinse solution and acidifies the rinse solution. The slightly acidic rinse solution attacks small amounts of oxides on the metal strip to further clean the metal strip surface. The rinse solution is preferably agitated to both facilitate the removal of the pickling solution from the metal strip and to dilute the removed pickling solution within the rinse solution. The agitators preferably include moving brushes which preferably contact the metal strip. The rinse solution is preferably recirculated and diluted to prevent the occurrence of high acidity levels.

[00172] In accordance with yet another aspect of the present invention, the metal alloy coating is applied to the metal strip by a hot-dip process. Some aspects of the hot-dip process may be used in various processes. Preferably, the coating of the metal strip is by a continuous hot dip process similar to the one disclosed in Assignee's U.S. patent application Ser. No. 000,101. The metal strip is coated in the hot-dip process by passing the metal strip at high speed through a coating tank which contains the molten alloy. The coating tank preferably includes a flux box whereby the metal strip passes through the flux box and into the molten alloy. The flux box preferably contains a flux which has a lower specific gravity than the molten metal alloy, thus the flux floats on the surface of the molten alloy. The flux within the flux box acts as the final surface treatment of the metal strip. The flux removes residual oxides from the metal strip surface, shields the metal strip surfaces from oxygen until the metal strip is coated with the molten metal alloy, inhibits the formation of viscous oxides at the

point where the metal strip enters the molten metal alloy and inhibits dross formation on the metal strip. In one embodiment, the flux preferably contains zinc chloride. In one embodiment, the flux also preferably contains ammonium chloride. In one embodiment, the flux solution contains approximately 30-60 weight percent zinc chloride and up to about 40 weight percent ammonium chloride and preferably 50% zinc chloride and 8% ammonium chloride; however, the concentrations of the two flux agents is varied accordingly.

[00173] In one embodiment, the coating tank is heated by heating coils, heating rods, gas jets, etc. Preferably, the coating tank is heated by at least one gas jet directed to at least one side of the coating tank. Heating coils and heating rods are preferably used to heat the metal directly in the coating tank which contains the tin alloy. Gas jets are used as an alternative to heating rods to heat the molten metal alloy, especially if the alloy includes large amounts of zinc. Such zinc containing alloys have been found to rapidly eat through the heating elements immersed in the alloy.

[00174] In one embodiment, a protective material is placed over the surface of the molten metal alloy in the coating tank. In one embodiment, the protective material has a specific gravity which is less than the molten metal alloy so that the protective material floats on the surface of the molten metal alloy. In one embodiment, the protective material shields the molten metal alloy from the atmosphere thereby preventing oxides from forming on the molten metal alloy surface. In one embodiment, the protective material also inhibits dross formation on the coated metal strip as the coated metal strip exits from the coating tank. When the protective material is palm oil, the melting point of the metal alloy must be below the 650° F. degrading point for the palm oil. For coating alloys having higher melting point temperatures, special oils, fluxes, or other materials and/or special cooling procedures for the protective material are employed.

[00175] In accordance with another aspect of the present invention, the continuously moving coated metal strip exiting the coating tank is subjected to an air-knife process. In an air-knife process, the coated metal strip is subjected to a high velocity gas. In one embodiment, the high velocity gas strips surplus molten metal alloy coating from the metal strip,

smears the molten metal alloy coating over the metal strip, improves the grain size of the metal alloy coating, reduces lumps or ribs of molten metal alloy coating forming on the surface of the metal strip and reduces the coating thickness of the molten metal alloy coating. In one embodiment, the high velocity gas is air or an inert gas which does not oxidize with the molten metal alloy. In one embodiment, the gas is an inert gas such as nitrogen, sulfur hexafluoride, carbon dioxide, hydrogen, noble gases and/or hydrocarbons. When an inert gas is used, the protective material on the surface of the molten metal alloy in the coating tank (i.e. palm oil) is preferably eliminated since the inert gas prevents dross formation, viscous oxide formation in the region in which the inert gas contacts the molten metal alloy in the coating tank. In one embodiment, the high velocity inert gas also breaks up and pushes away any dross or viscous oxides from the surface of the molten metal alloy in the coating tank in the region the inert gas contacts the molten metal alloy thereby forming an essentially dross free-viscous oxide free region for the coated metal strip to be removed from the coating tank. In one embodiment, the high velocity gas is preferably directed onto both sides of the coated metal strip and at a direction which is downward toward the coating tank and at a direction which contacts the coated metal strip at an angle which is not perpendicular to the surface of the coated metal strip. In one embodiment, the direction of the gas directs the removed molten metal coating alloy back into the coating tank. An applicable design of the air knife process is disclosed in U.S. Pat. No. 4,862,825 which is incorporated herein.

[00176] In one embodiment, the thickness the molten metal alloy coating is controlled by one or more sets of coating rollers. In one embodiment, the coating rollers form a smooth and uniform metal alloy coating layer on the metal strip. When palm oil is used as a protective material on the surface of the coating tank, the coating rollers are preferably partially or totally immersed in the palm oil. In one embodiment, the palm oil facilitates in quality distribution of the metal alloy coating layer onto the metal strip. In one embodiment, the thickness of the metal alloy coating is at least 0.0001 inch and is preferably 0.0003-0.05 inch and more preferably, 0.001-0.002 inch. The thickness of the metal alloy coating is also regulated by the residence time of the metal strip in the coating tank, the temperature of the

metal alloy in the coating tank and the use of an air-knife process. In one embodiment, the thickness of the alloy coating coated on the metal strip will also be dependent on the speed at which the metal strip travels through the alloy. In one embodiment, a strip speed above 400 ft/min results in high shear forces which interferes with proper coating resulting in improper or defective alloy coating of the metal strip. When an air-knife process is employed, the coating rollers are preferably used in conjunction with the air-knife process or alternatively, the coating rollers are completely eliminated.

[00177] In one embodiment, spray jets are preferably used to spray molten metal alloy onto the metal strip to ensure a uniform and continuous coating on the metal strip. In one embodiment, the metal spray jets are preferably positioned adjacent to the coating rollers to ensure complete coating of the metal strip. In one embodiment, the metal spray jets spray molten metal alloy onto the coating rollers and/or onto the metal strip. As the coating rollers rotate to allow the metal strip to pass between the coating rollers, the molten metal alloy sprayed on the rollers is pressed against the metal strip and fills in any pin holes or uncoated surfaces on the metal strip. The use of spray jets eliminates the need for two separate coating steps, especially when the invention is used for tin coating. When coating rollers are not used, spray jets are preferably used to spray the molten metal alloy directly onto the metal strip.

[00178] In one embodiment, after the metal strip has been coated, the coated metal strip is preferably cooled. In one embodiment, the cooling of the coated metal strip is accomplished by spraying the coated metal strip with a cooling fluid such as ambient temperature water and/or immersing the coated metal strip in a cooling liquid such as ambient temperature water. In one embodiment, the cooling of the coated metal strip usually is less than one hour and preferably is less than a few minutes. When the alloy coating cools at different rates, different grain size and grain densities are formed. Slowly cooling the alloy coating results in larger grain size, lower grain densities, and a highly reflective surface. Rapid cooling of the alloy coating produces fine grain size, increased grain density and a less reflective surface. Small grain sizes and higher grain densities produce a

stronger bond with the metal strip and greater corrosion resistance. For a liquid injection or spray process, water is jet sprayed onto the coated metal strip. In such a cooling process, the metal strip is preferably guided through the cool water jet sprays by a camel-back guide. The camel-back guide is designed such that only the edges of the coated metal strip contact the guide. By minimizing the contact of the coated metal strip with the guides, the amount of coating alloy inadvertently removed from the coated metal strip is reduced. The camel-back guide is also designed to allow the water jets to cool the underside of the coated metal strip. For an immersion process, the cooling water is normally agitated to increase the cooling rate of the coating metal strip. The temperature of the cooling water is preferably maintained at proper cooling temperatures by recycling the water through heat exchangers and/or replenishing the water. The cooling water is preferably not deoxygenated prior to cooling the coated metal strip coating. The oxygen in the cooling water oxidizes with the metal coating alloy during rapid cooling which results in a slightly discolored coated metal strip surface having reduced reflectability.

[00179] In one embodiment, the coated metal strip is passed through a leveler, whereby the coated metal alloy is uniformly molded about the metal strip. In one embodiment, the leveler consists of a plurality of rollers. The coated metal strip is passed through the rollers to smooth out the metal alloy coating on the metal strip. In one embodiment, the metal strip is preferably maintained at a tension as it is passed through the leveler.

[00180] In one embodiment, the coated strip is coiled into coils for later processing on high speed presses, such as used in the automotive field. Alternatively, the coated metal strip is sheared after it has been cooled or leveled. Since the metal strip is a continuously moving metal strip, the shearing device travels next to and at the same speed as the coated metal strip to properly shear the moving strip. When the metal strip is not cut, the metal strip is rolled into a roll of coated strip for ease of transport and/or for use in subsequent treatments and/or forming (i.e. roof materials). In one embodiment, the continuous processing of the strip from roll to roll facilities in the ease, efficiency and cost effectiveness of coating a metal strip.

[00181] In one embodiment, the metal strip is processed in an acid solution after coating the metal strip to expose the intermetallic layer which formed between the metal strip surface of the strip and the coating alloy during the hot dip coating process. The removal of the layer of metal alloy coating is described in Assignee's Application Serial No. 165,085 which is incorporated herein.

[00182] In one embodiment, the coated metal strip is treated with a weathering agent to accelerate the weathering and discoloration of the metal alloy coating. Metal alloy coatings containing high concentrations of tin are commonly highly reflective. To reduce the reflectivity of such metal alloy coatings, the weathering material is applied to the metal alloy coating to oxidize the metal alloy coating surface and reduce the reflectivity of the metal alloy coating. In one embodiment, the weathering material is an asphalt-based paint which causes accelerated weathering of the metal alloy coating when it is exposed to the atmosphere. In one embodiment, the asphalt-based paint significantly decreases the weathering time of the metal alloy coat to less than a year. In one embodiment, the asphalt paint is preferably a petroleum-based paint which includes asphalt, titanium oxide, inert silicates, clay, carbon black or other free carbon and an anti-settling agent. In one embodiment, the asphalt-based paint is preferably applied at a relatively thin thickness so as to form a semi-transparent or translucent layer over the metal alloy coating. The thickness of the asphalt-based paint ranges between 0.25 to 5 mils and preferably is 1-2 mils. Once the translucent paint has been applied to the coated metal strip, the weathering material is dried, preferably by air drying and/or heated by heating lamps.

[00183] In one embodiment, the metal alloy coating composition is such that the coated metal strip is formed on site without the metal alloy coating cracking and/or flaking off. For zinc containing alloys, the amount of zinc is controlled and stabilizers are used to prevent the coating alloy from becoming too rigid and brittle and to also inhibit the formation of zinc oxide.

[00184] In one embodiment, the strip is provided in a large coil, passed through a pretreatment process, usually without preheating, and then moved

continuously as a continuous moving strip through the bath containing a metal coating alloy.

[00185] In one embodiment, a thin ferrous strip is uncoiled and passed longitudinally through a molten bath of a coating alloy comprising at least about 15% by weight tin at a speed so that an intermetallic layer is formed between the coating alloy and the surface of the ferrous strip. When the thin strip includes chromium, as well as iron, it is defined as a "stainless steel" strip. In one embodiment, the thin strip is continuously passed through an electrolytic tank to coat an ultra thin layer of tin, chromium, nickel or copper on the moving strip prior to hot dip coating. This coating or "flashing" of tin chromium, nickel or copper does not interfere with the formation of intermetallic layer and improves the bonding and corrosion resistance of the coating alloy.

[00186] In one embodiment, when flashing on tin, the tin is heated to cause it to flow before or during the subsequent hot dip coating process.

[00187] In one embodiment, the metal alloy exhibits excellent soldering characteristics such that various electrodes including lead and no-lead electrodes can be used to weld the coated metal.

[00188] In one embodiment, the flux for hot dip galvanization in accordance with the invention comprises: 60 to 80 wt. % (percent by weight) of zinc chloride (ZnCl2); 7 to 20 wt. % of ammonium chloride (NH4 Cl); 2 to 20 wt. % of at least one alkali or alkaline earth metal salt 0.1 to 5 wt. % of a least one of the following compounds: NiCl2, CoCl2, MnCl2 ; and 0.1 to 1.5 wt. % of at least one of the following compounds: PbCl2, SnCl2, SbCl3, BiCl3.

[00189] Such a flux, wherein the different percentages relate to the proportion in weight of each compound or compound class relative to the total weight of the flux, makes it possible to produce continuous, more uniform, smoother and void-free coatings on iron or steel articles by hot dip galvanization with zinc-aluminum alloys, especially in batch operation. The selected proportion of ZnCl2 ensures a good covering of the article to be galvanized and effectively prevents oxidation of the article during drying of the article, prior to the galvanization. The proportion of NH4 Cl is

determined so as to achieve a sufficient etching effect during hot dipping to remove residual rust or poorly pickled spots, while however avoiding the formation of black spots, i.e. uncovered areas of the article. In one embodiment, the alkali or alkaline earth metals, in the form of salts, are employed to modify the activity of the molten salts, as will be detailed below. The following compounds: NiCl2, CoCl2, MnCl2, are believed to further improve by a synergistic effect the wettability of steel by molten metal. The presence in the flux of between 0.1 to 1.5 wt. % of at least one of PbCl2, SnCl2, BiCl3 and SbCl3 permits to improve the wetting of an iron or steel article, covered with this flux, by molten zinc in a galvanizing bath. Another advantage of the flux of the invention is that it has a large field of applicability. As mentioned, the present flux is particularly suitable for batch hot dip galvanizing processes using zinc-aluminum alloys but also pure zinc. Moreover, the present flux can be used in continuous galvanizing processes using either zinc-aluminum or pure zinc baths, for galvanizing e.g. wires, pipes or coils (sheets). The term "pure zinc" is used herein in opposition to zinc-aluminum alloys and it is clear that pure zinc galvanizing baths may contain some additives such as e.g. Pb, Sb, Bi, Ni, Sn.

[00190] In one embodiment, the proportion of zinc chloride is between 70 and 78% by weight relative to the total weight of the flux. In one embodiment, the ammonium chloride is in a proportion of 11 to 15% by weight. In one embodiment, the NiCl2 content in the flux is preferably of 1% by weight. In one embodiment, the flux further comprises 1% by weight of PbCl2.

[00191] Referring more specifically to the alkali or alkaline earth metals, they are advantageously chosen from the group (sorted in decreasing order of preference) consisting of: Na, K, Li, Rb, Cs, Be, Mg, Ca, Sr, Ba. In one embodiment, the flux comprise a mixture of these alkali or alkaline earth metals, as they have a synergistic effect which allows to control the melting point and the viscosity of the molten salts and hence the wettability of the surface of the article by the molten zinc or zinc-aluminum alloy. They are also believed to impart a greater thermal resistance to the flux. In one embodiment, the flux comprises 6% by weight of NaCl and 2% by weight of KCl.

[00192] In one embodiment, a fluxing bath for hot dip galvanization is proposed, in which a certain amount of the above defined flux is dissolved in water. The concentration of the flux in the fluxing bath may be between 200 and 700 g/l, preferably between 350 and 550 g/l, most preferably between 500 and 550 g/l. This fluxing bath is particularly adapted for hot dip galvanizing processes using zinc-aluminum baths, but can also be used with pure zinc galvanizing baths, either in batch or continuous operation.

[00193] In one embodiment, the fluxing bath should advantageously be maintained at a temperature between 50 and 90° C., preferably between 60 and 80° C., most preferably of 70° C.

[00194] In one embodiment, the fluxing bath may also comprise 0.01 to 2 vol. % (by volume) of a non-ionic surfactant, such as e.g. Merpol HCS from Du Pont de Nemours, FX 701 from Henkel, Netzmittel B from Lutter Galvanotechnik Gmbh or the like.

[00195] In one embodiment, a process for the hot dip galvanization of an iron or steel article is proposed. At a first process step (a), the article is submitted to a degreasing in a degreasing bath. The latter may advantageously be an ultrasonic, alkali degreasing bath. Then, in a second step (b), the article is rinsed. At further steps (c) and (d) the article is submitted to a pickling treatment and then rinsed. It is clear that these pre-treatment steps may be repeated individually or by cycle if needed. In one embodiment, the whole pre-treatment cycle (steps a to d) is preferably carried out twice. It shall be appreciated that at the next step (e) the article is treated in a fluxing bath in accordance with the invention so as to form a film of flux on the article's surface. In one embodiment, the article may be immersed in the fluxing bath for up to 10 minutes, but preferably not more than 5 minutes. In one embodiment, the fluxed article is subsequently dried (step f). At next step (g), the article is dipped in a hot galvanizing bath to form a metal coating thereon. The dipping time is a function of size and shape of the article, desired coating thickness, and of the aluminum content (when a Zn--Al alloy is used as galvanizing bath). Finally, the article is removed from the galvanizing bath and cooled (step h). This may be carried out either by dipping the article in water or simply by allowing it to cool down in the air.

[00196] In one embodiment, the present process is particularly well adapted for the batch hot dip galvanizing of individual iron or steel articles, but also permits to obtain such improved coatings with wire, pipe or coil material continuously guided through the different process steps. More over, pure zinc galvanizing baths may also be used in the present process. Accordingly, the galvanizing bath of step (g) is advantageously a molten zinc bath, which may comprise from 0 to 56% by weight of aluminum and from 0 to 1.6% by weight of silicon. More specifically, this means that well known alloys such as: SUPERGALVA® a registered trademark of Mitsui Mining & Smelting Co. Ltd., Japan, containing essentially 3-7 wt. % Al, 0-3 wt. % Mg, 0-0.1 wt % Na, rest Zn; GALFAN®, a registered trademark of International Lead Zinc Research Organization, Inc., containing essentially 4.2-7.2 wt. % Al, 0.03-0.10 wt. % mischmetals, rest Zn; or GALVALUME®, a registered trademark of BIEC International, Inc., containing essentially 55 wt. % Al, 1.6 wt. % Si, rest Zn; may be used as galvanizing baths.

[00197] In one embodiment, the galvanizing bath is preferably maintained at a temperature between 380 and 700° C.

[00198] At step (f) the article is preferably dried in a forced air stream heated at a temperature between 200 and 350° C., more preferably 250° C. In one embodiment, the surface of the article shall exhibit a temperature between 170 and 200° C. before being dipped into the galvanizing bath at step (g). This is possible as the fluxing bath of the invention has a high thermal resistance and is effective for limiting corrosion of the article. Preheating the article before step (g) facilitates the remelting of the frozen metal layer which forms on the surface of the article directly after immersion in the galvanizing bath.

[00199] For the same purpose of remelting the frozen metal layer, the article is advantageously moved in the galvanizing bath during at least the first minutes following its introduction therein. In one embodiment, the agitation should be stopped before the removal of the article from the galvanizing bath to avoid deposition on the article's surface of dirt and scum overlying the galvanizing bath. Generally, the thicker and voluminous the article, the more intense the agitation. In one embodiment,

an inert gas, such as e.g. nitrogen (N2) or argon (Ar), may be introduced into the galvanizing bath, preferably in the form of fine bubbles, so as to obtain a bubbling effect.

[00200] It shall be noted that the present process is adapted to galvanize steel articles made of a large variety of steels. In one embodiment, steel articles having a carbon content up to 0.25 wt. %, a phosphorous content between 0.005 and 0.1 wt. % and a silicon content between 0.0005 and 0.5 wt. % may be galvanized with the present process. According to another aspect of the invention, a hot dip galvanizing bath is proposed. It comprises: up to 56 wt. % of Al; from 0.005 to 0.15 wt. % of Sb and/or from 0.005 to 0.15 wt. % of Bi; maximum 0.005 wt. % of Pb, maximum 0.005 wt. % of Cd and maximum 0.002 wt. % of Sn; and the rest being essentially Zn.

[00201] Such a galvanizing bath permits to obtain improved coatings on iron or steel articles. In one embodiment, the presence of selected concentrations of Sb and/or Bi in this galvanizing bath, combined with the limitation on the concentrations of Pb, Cd and Sn, is believed to improve the resistance to the formation of white rust and to intergranular corrosion of the obtained coatings. This is particularly observed when the aluminum content is between 2 and 56 wt. %. Moreover, obtained coatings are smooth and have an attracting appearance. This galvanizing bath is particularly well suited to be used in the process of the invention.

[00202] As indicated, Sb or Bi, which are supposed to have the same effect in the galvanizing bath, may be present in the bath separately or together in the prescribed amounts. However, a concentration from 0.005 to 0.04% by weight of Sb is preferred.

[00203] In another embodiment, the galvanizing bath is based on the composition of GALFAN®, to which Bi and/or Sb is/are added in accordance with the above prescribed amounts. Accordingly, the galvanizing bath comprises (in proportions by weight): 4.2-7.2% of Al, 0.005-0.15% of Sb and/or 0.005 to 0.15% of Bi, max. 50 ppm of Pb, as well as 0.03-0.10% of mischmetals, max. 150 ppm of Si, max. 750 ppm of Fe, max. 50 ppm of Cd, max. 20 ppm of Sn, with the remainder being essentially Zn, these proportions of Si, Fe, Cd and Sn being typical for GALFAN®. The

galvanizing bath may also contain small amounts of Mg, Cu, Zr or Ti. It shall however be noted that, contrary to conventional specifications of GALFAN®, this galvanizing bath should preferably comprise: no more than 10 ppm, more preferably no more than 5 ppm, of Sn; no more than 25 ppm, more preferably no more than 12 ppm, of Pb; no more than 25 ppm, more preferably no more than 12 ppm of Cd. Indeed, these compounds are believed to promote intergranular corrosion. Furthermore, the galvanizing bath should comprise no more than 500 ppm, more preferably no more than 150 ppm of Mg. The limitation on the Mg content enhances the surface aspect of the finished products.

[00204] Although this invention has been described in connection with its most preferred embodiment, additional embodiments are within the scope and spirit of the claimed invention. The preferred device of this invention is intended merely to illustrate the invention, and not limit the scope of the invention as it is defined in the claims that follow.

[00205] EXAMPLES

[00206] **Example 1.**

[00207] **Materials**

[00208] The bath is made up by melting ingots of the master alloys Zn23Al and Zn23Al3Si, which is prepared by the Teck Cominco Product Technology Centre (Mississauga, ON, Canada), hereinafter referred to as PTC. They are melted in such ratios that a bath analysis of 23 wt.-% Al and 0.2-0.7 wt.-% Si is obtained.

[00209] The steels that are tested consist of a variety of cold-rolled and hot-rolled carbon steel panels of 75×105 mm and 2.5 mm thickness. In addition, a series of well-characterized steels is galvanized, whose silicon and phosphorus contents are listed in Table 1. Their thickness is also 2.5 mm. It is seen that the silicon levels varied by a factor of 11 and under conventional galvanizing conditions using typical HDG bath alloys considerable differences in coating thickness are obtained at PTC. A third set of materials consisted of small sections of I-beam, tubes, and angle bars, etc., which are dipped in a larger laboratory crucible (see next

section). The purpose of these experiments is to study the behavior of the flux in galvanizing more complex shapes.

TABLE 1. C, Si and P levels of characterized set of steels

Steel No.	wt.-% C	wt.-% Si	wt.-% P
2	0.09	0.03	0.003
3	0.09	0.13	0.003
4	0.09	0.17	0.003
7	0.09	0.35	0.003
10	0.09	0.087	0.052

[00210] **Cleaning**

[00211] Prior to fluxing, all samples are cleaned in an alkaline degreaser for 10 min. at 70°C, which is followed by a 20-25 min. dip at 25°C in an acid cleaner. The panels are then thoroughly rinsed in DI water and fluxed.

[00212] **Fluxing**

[00213] The Cu-Sn flux [6,7] is not used in this project. A flux based on the conventional zinc-ammonium chloride flux is used, which had been modified for use with Al-containing zinc baths.

[00214] Immediately after cleaning, the steels are fluxed in this solution for 2 min. at 55°C and then dried at 100°C for 10-15 min. They are typically galvanized within 15 min. after fluxing.

[00215] **Bath Preparation and Dipping**

[00216] For the small panels a 30-kg laboratory silicon carbide crucible is used. The larger samples are immersed into a 500-kg crucible. The fluxed panels are hung on a wire and inserted into the bath at a constant speed of 60 cm/min using a pneumatic insertion device. This speed is not varied in this project. The baths are made up from the two master alloys and then first analyzed for silicon and aluminum levels. After galvanizing a certain number of panels the bath is replenished by adding very small chunks of the master alloys, so as not to lower the bath temperature too much. In general, the parameters that are varied in these experiments are the

immersion time, the bath temperature, the silicon level of the bath and the steel quality. The flux and fluxing process, the immersion speed, the bath composition – other than the silicon level – or the preheating of the panels, are not varied in the experiments reported here.

[00217] **Bath Analysis**

[00218] The bath is analyzed for Zn, Al, Si and Fe levels at regular intervals. Standard ICP techniques are used with the results becoming available within four hours.

[00219] **SEM/EDX of Cross Sections**

[00220] Cross sections of the coating are analyzed by cross cutting, mounting in resin and then polishing. The cross sections are etched in Nital and then inspected in a Scanning Electron Microscope equipped with Energy-Dispersive X-Ray analysis. Both a JEOL JSM 5800LV equipped with an EDX type PGT PRISM instrument at PTC and a Philips ESEM model XL-30 microscope at the University of Cincinnati are used. Of some samples secondary electron images of the surface are also taken.

[00221] **Corrosion Testing**

[00222] Panels are exposed to a salt fog as per the ASTM B-117 standard. They are placed in a rack at 45°. The edges are not taped. The criterion for failure is the appearances of traces of red rust, not white rust. When red rust appeared, the panels are removed from the test. They are then washed in DI water, photographed and cleaned in order to remove the voluminous amounts of white rust formed on the surface. The cleaning procedure used is in accordance with the ASTM G1 specification (C.9.2 and C.9.5). They are then photographed again. In other exposures, the degree of weight loss in the test is monitored rather than red rust appearance. The weight loss is compared with that of conventional hot-dip galvanized panels, kindly provided by the Weert Groep in The Netherlands, and with panels dipped into a Zn5Al bath of 450°C at PTC. In the latter set of experiments the same steels are used as for the Zn23Al0.3Si experiments. In the case of the panels received from the Weert Groep, the steel type is unknown.

[00223] In another set of experiments the galvanized panels are bent in a vise by 180° and then exposed in the B-117 test. The purpose of this experiment is to verify the ductility of the Zn23Al0.3Si coating. If the coating would not withstand the bending process, red rust is expected to appear on the bend before it would appear on the non-bent surfaces. Regular HDG and Zn5Al coatings are used as controls in this experiment.

[00224] In a final set of experiments, a deep diagonal scribe is machined in the coating and into the base steel using a sharp-edged SiC cutting wheel. The purpose here is to test the cathodic protection capability of the coating. It is known that aluminum coatings do not provide much cathodic protection, as they easily passivate spontaneously. Diluting zinc with aluminum therefore reduces the cathodic protection capability of the zinc coating. This is, for instance, observed in Galvalume® which has a poor edge corrosion resistance because of this effect. Here, too, conventional HDG and Zn5Al coatings are used as controls.

[00225] **Electrochemical Testing**

[00226] The electrochemical activity of the surface of the coatings is measured by performing potentiodynamic polarization tests in an aerated 3.5 wt.-% NaCl solution. The potentiostat used is a Gamry CMS100 system equipped with an SR810 Frequency Response Analyzer. The counter electrode is a platinum mesh and a saturated calomel electrode (SCE) is used as the reference electrode. Both cathodic and anodic curves are recorded. It should be noted that the corrosion cell used in these measurements is a so-called flat cell, in which a large panel is clamped against a hole of about 1 cm^2 at one end of the cell. The electrolyte only contacted the sample through this hole. In this set-up any cutting and possible delamination effects are avoided. Further, cut samples would have edge effects due to exposed steel at the edges. The IR drop effect, inherent in the use of a flat cell, is automatically compensated by the potentiostat. Along with the Zn23Al0.3Si coatings, controls of standard HDG and delta-galvanized steel (both provided by the Weert Groep on unknown steels), and Zn5Al, prepared at PTC, are also tested.

[00227] It should be pointed out here that the results of these electrochemical tests indicate the initial electrochemical reactivity (dissolution rate in NaCl)

only. The results of the B-117 test, described above, are different in that they indicate the resistance against red rusting only. The polarization tests is quantified to give the corrosion rate which is the rate of the consumption of the alloy coating in the solution. The results of these two tests do not necessarily have to agree.

[00228] **Hardness Measurements**

[00229] The hardness of the new coatings is estimated in cross sections using a Leco 400 micro-hardness device. This allows one to estimate the hardness of the two layers that are normally detected in the coatings.

[00230] **RESULTS AND DISCUSSION**

[00231] **Experiments with the Cu-Sn and a Zinc Ammonium Chloride Flux**

[00232] The Cu-Sn flux [6] is initially tried for the bath composition Zn23Al0.3Si at about 550°C, but failed to produce coatings without outbursts or bare spots, regardless of the dipping time, dipping temperature, immersion rate or preheating temperature. The modified flux, based on zinc ammonium chloride, developed for the Zn5Al alloy, worked surprisingly well and formed practically outburst-free coatings in the range of 550-600°C that is initially tested. Thus, this flux is used in all experiments discussed in this paper. The treatment time and temperature are kept constant.

[00233] **Coating Structure**

[00234] The surface of the coatings produced at 0.3% Si is smooth and generally does not show clear spangles. In the electron microscope, the secondary electron images (s.e.) of the surface shows either an interdendritic phase system or two distinct phases, as shown in Figure 2. This two-phase system is typically found for thinner panels that are cooled rapidly or galvanized at lower temperatures. Therefore, the primary, or alpha phase, of this two-phase system is suspected to be the eutectoid composition (Zn/Al = 77/23) Al-rich phase, that is formed upon cooling below 406°C. The coarser secondary phase is formed from the remaining liquid resulting in eutectic phase. This interdendritic phase should disappear at 348°C, but if the cooling rate is fast, it still exists in a metastable form at the eutectoid temperature of 270°C. Annealing the parts at temperatures between 275°C

and 350°C should convert the coating to the eutectoid composition if desired. At this point of our investigations, it is not known if the presence of that Al-rich interdendritic phase is beneficial or not. It could be envisioned that if one needs the ultimate mechanical properties in terms of plasticity, such annealing is warranted, e.g., of small parts, such as fasteners.

[00235] Figure 3 also depicts s.e. images of cross sections taken from samples produced at various operating conditions. Figure 3a shows a coating exhibiting two continuous layers. The thin layer at the metal-coating interface is found to contain measurable levels of Fe, Al, Si and Zn and therefore will be denoted as $Fe_{2-x-y}Al_5Zn_xSi_y$, with x and y as variables such that $x+y<1$. This layer is continuous and uniform with a thickness between 5-10 μm. The top layer is also uniform and has approximately the bath composition, so it is interpreted as the drag-out layer of the bath. Under magnification it becomes apparent that this layer exhibits a distinct lamellar structure. Thus, it must be composed of the two phases into which the eutectoid composition decomposes, initially Zn/Al = 31/68 and 99/1 (Figure 1), but, depending on the cooling rate experienced, the Al-rich phase iscome richer in Al, as is concluded from Figure 1. Figure 3b shows a sample in which regions with the eutectoid composition are embedded in another phase, namely the phase seen in Figure 2b from the top. This is an Al-rich interdendritic phase which has not been completely converted to the two phases with rather narrow composition which narrows further when approaching the eutectoid, i.e., around Zn/Al = 75/25 and Zn/Al = 80/20 (Figure 1). In the eutectoid phase the lamellar structure is still clearly discerned.

[00236] The Si is found to be distributed throughout the entire coating. However, its level in the $Fe_{2-x-y}Al_5Zn_xSi_y$ phase is higher than the overall bath composition. We can, therefore, conclude that, indeed, the Si in the bath stabilizes the $Fe_{2-x-y}Al_5Zn_xSi_y$ layer, as the entire coating is devoid of Fe-Zn outbursts. As a result, the coating is of a simple structure, viz., that of a solidified drag-out layer on top of a reaction layer formed by the reaction of steel with the aluminum in the bath. Even in the case of a multiphase drag-out layer, the intermetallic layer remains continuous and does not

vary significantly in thickness. Because that layer is formed at the high temperature of the liquid bath and further growth then seems to stop it is self-limiting and only varies in thickness as a function of the bath temperature (see below). It is therefore suggested that the structure of the $Fe_{2-x-y}Al_5Zn_xSi_y$ layer is not much dependent on the cooling rate, whereas the structure of the drag-out layer is.

[00237] **Effect of Dipping Conditions**

[00238] The effect of dipping time, dipping temperature and silicon level of the bath is investigated in order to better understand the formation of the two layers shown in Figure 3. More studies will be performed for a more complete kinetic analysis. The following observations are made.

[00239] **Effect of dipping time**

[00240] At 575°C and 0.18 wt.-% Si the thickness of the interfacial layer increased parabolically with time, whereas that of the outer layer remains constant. An example of layers obtained after 1 min. and 10 min. dipping time is shown in Figure 4.

[00241] **Effect of dipping temperature**

[00242] At 0.4 wt.-% Si the thickness of the inner layer increased approximately linearly with the temperature for 1 min. dipping time. The range of 550°C to 600°C is investigated here. The thickness of the outer layer remains constant until 575°C and then decreases.

[00243] **Effect of bath levels of silicon**

[00244] So far, the range of 0.18 to 0.75 wt.-% has been investigated. Below 0.18 wt.-% the coating formation is uncontrolled due to the outbursting effect. In the range of 0.18 to about 0.7 wt.-%, the thickness of both inner and outer layer layer does not change significantly. This is observed for several temperatures in the range of 550-600°C and for all dipping times. At 0.75 wt.-%, the thickness of the inner layer decreases sharply, but does not disappear completely. The thickness of the outer layer does not vary with silicon level.

[00245] These observations is accommodated in a simple model for coating formation. The outer layer is clearly a drag-out layer only. It may vary in terms of phase separation, depending on the cooling rate, but its thickness is only dependent on the dipping temperature. The higher the temperature, the lower the viscosity and the thinner the layer will be. The withdrawal speed will probably also affect the layer thickness. The inner layer is clearly a reaction layer and is diffusion-controlled. Iron diffuses outward and reacts with aluminum in the bath. Thus, longer dipping times and higher temperatures will increase the thickness of the inner layer. However, since the growth is parabolic, the thickness levels off with dipping times. As a result of the two opposite effects of the temperature for the two layers, the overall thickness is generally not greater than 30 μm. Thinner, continuous layers is obtained, however, by adjusting the dipping time, temperature and/or silicon level. We have obtained good-quality coatings as thin as 10 μm or less.

[00246] The silicon level is very important in this process. At lower levels, it suppresses the outbursting effect effectively. Then there is a range of about 0.5 wt.-% (range 0.2-0.7 wt.-%) where there is no effect on either layer thickness. At levels higher than 0.7 wt.-%, it seems that other reactions begin to dominate and the iron-aluminum reaction is impaired. It is suspected that iron then reacts with silicon directly, forming an interfacial layer of $FeSi_2$, as in Galvalume®, which hampers the outward diffusion of iron. However, we only have indirect evidence for this reaction. More studies of the kinetics using well-characterized steels of widely different compositions are in progress.

[00247] In summary of this section, the parameters dipping time, dipping temperature and silicon level could be used in a controlled way to vary the properties of the coating systems such as hardness, wear resistance, corrosion resistance, etc. It is envisaged that a bath for fasteners is run under conditions different from a bath used for larger parts such as I-beams or guard rails. For fasteners a thin, hard, wear-resistant coating would be obtained at high temperature and longer dipping times. For the larger parts, both the temperature and dipping times could be lowered.

[00248] **Effect of Si Level of the Steel**

[00249] The set of steels with known Si and P levels (Table 1) are dipped at 575°C for 5 min. in a bath with 0.4 wt.-% Si. They are cooled in ambient conditions and cross-sectioned. Some results in terms of s.e. images and EDX results are presented in Figures 5 and 6. The following conclusions is drawn from the results.

[00250] The total coating thickness is 25-30 μm. There is no effect of the silicon or phosphorus content on the total layer thickness. Since most of the layer is the solidified drag-out layer, such an effect could not be expected. The thickness of the reaction layer under the drag-out layer is also constant and is in most cases around 5-10 μm.

[00251] The drag-out layer is similar in all cases and is fairly continuous with occasional evidence for the Al-rich interdendritic layer mentioned earlier. This layer does not seem to depend on the steel composition.

[00252] The silicon content of the interfacial reaction layer is in all cases higher than that of the bath, viz., up to about 8 wt.-%. Again, there is no clear trend with the steel composition. The Si content of the drag-out layer is around the bath composition or slightly lower, as is expected. The Si content of the interdendritic layer varies, but is, on average, similar to that of the eutectoid layer.

[00253] In the steels with either the high Si (0.35 wt.-%) or P (0.052 wt.-%) content, the interfacial reaction layer is no longer continuous. Although the thickness remains the same, there are regions where that layer is broken up or missing. Apparently, the high Si or P level blocks the reactivity of the steel to the Al of the bath. This is only a local effect and whether it affects the mechanical or corrosion properties of the coatings has not yet been investigated.

[00254] In summary, these results show that the Sandelin effect associated with general galvanizing does not play a role when the Zn23Al0.3Si bath is used. Many qualities of steel is effectively coated without effect on coating thickness or performance.

[00255] **Corrosion Properties**

[00256] Since the development of a novel coating for general galvanizing is prompted by the need for a more corrosion-resistant alloy coating that would lower the rate of zinc run-off into the environment, the results shown in this section are of great importance in determining whether this project is successful or not. The results with the Zn23Al0.3Si alloy are, in all tests that have so far been performed, vastly superior to those obtained with the convention HDG control and also superior to those obtained with the Zn5Al system.

[00257] **Salt spray resistance**

[00258] Figure 7 shows panels of regular HDG and Zn23Al0.3Si panels after exposure in the B-117 test. The HDG is removed after 350 hours, the Zn23Al0.3Si after 2000 hours. The HDG panel had begun to form red rust, clearly seen in the Figure. One of the Zn23Al0.3Si panels also shows one spot of red rust after 2000 hours, so the test is terminated. Panels of Zn5Al (not shown) lasted about 600 hours in this test before red rust appeared. Thus, the Zn5Al coatings are a factor of 2 better than HDG, the Zn23Al0.3Si coating is a factor 6-7 better, at least in this test. It should be noted that the coating thickness of the HDG panels is 75 μm, whereas that on both the Zn5Al and Zn23Al0.3Si is not more than 25-30 μm. The results illustrate the enormous effect that Al has on the protection against red rust.

[00259] **Weight loss measurements**

[00260] Figure 7 shows copious amounts of white rust that had been formed on both the HDG and the Zn23Al0.3Si panels in the salt spray exposure. One could argue that the corrosion resistance of Zn23Al0.3Si is only due to the interfacial reaction layer of iron-aluminides and that the corrosion resistance of the drag-out layer is similar to that of conventional HG. Therefore, the weight loss in the salt spray test is measured quantitatively in another comparative test involving HDG, Zn5Al and Zn23Al0.3Si. The results are shown in Table 2, which also lists the coating thicknesses for these materials. It is seen that Zn5Al loses, on average, 1.6 g/24 days, HDG loses 2.5 g/14 days and Zn23Al0.3Si loses only 0.46 g/24 days. On a daily basis these weight loss ratios are 1 : 3 : 9 for Zn23Al0.3Si, Zn5Al and HDG, respectively. These ratios are similar to the red rust appearance

data reported above and they demonstrate that it is not only the interfacial iron-aluminide layer but the Zn-Al drag-out layer as well that contributes to the outstanding corrosion resistance of Al-containing coatings, especially the Zn23Al0.3Si system.

TABLE 2. Weight loss in salt spray testing of HDG, Zn5Al and Zn23Al0.3Si coatings

Coating	Thickness, μm	Days in B-117	Weight Loss, g
HDG	70	3	0.830
HDG	75	3	0.961
HDG	55	14	2.548
HDG	55	14	2.487
Zn5Al	5	24	1.457
Zn5Al	20	24	1.828
Zn23Al0.3Si	20	14	0.288
Zn23Al0.3Si	10	14	0.225
Zn23Al0.3Si	15	24	0.476
Zn23Al0.3Si	15	24	0.465

[00261] Bend test

[00262] In another test, panels of the three coating systems are bent in a vise over 180° and then exposed in the salt spray chamber again. The purpose is to verify whether the Zn23Al0.3Si system is, indeed, ductile. The performance criterion in this test is the appearance of red rust in the bend, i.e., the region of the highest tensile stresses. The HDG panels are exposed for only 3 days, as red rust had already become apparent. The Zn5Al and Zn23Al0.3Si panels are exposed for 24 days. The results are shown in Figure 8. It is observed that the HDG panel shows a large amount of white rust and has also formed red rust in the bend area. The Zn5Al panel began to break down as it shows local spots of red rust. The Zn23Al0.3Si panel shows less white rust than the other systems and not a single spot of red rust. Thus, it is concluded that this coating can withstand severe deformations better than HDG and Zn5Al.

[00263] In order to check on the deformability of the Zn23Al0.3Si coating further, cross sections are prepared of the 180°-bent panels, which are then analyzed in the electron microscope. The results are shown in Figure 9. It is seen that on the compression side of the panel the coating is not cracked. On the tensile side of the deformed panel – which is the side exposed in the B-117 test – it is observed that the drag-out layer has not cracked, but has become considerably thinner. The interfacial reaction layer has not deformed, but has cracked. These results confirm that the Zn-Al drag-out layer is very ductile and that the iron-aluminide layer is not. However, the corrosion performance does not suffer in the bend test, due to the strong protective action of the top layer.

[00264] **Scribe test**

[00265] HDG can protect steel by cathodic protection of the steel exposed in a defect, as has been well documented. In this test, the cathodic protection performance of the new Zn23Al0.3Si system is investigated. It could be argued that Al by itself does not protect steel, as it tends to passivate. Hence, diluting zinc with aluminum could lead to a degradation of the cathodic protection effect. Panels are scribed with a SiC cutting wheel, so that the scribe extended into the base steel. The panels are then exposed in the B-117 test. This test is performed with HDG and Zn23Al0.3Si only, which are exposed for 14 and 24 days, respectively. The scribed and tested panels are shown in Figure 10, which also shows the panels after cleaning in an acid. One can notice the difference in white rust formation between the two, although the Zn23Al0.3Si system is exposed for almost twice as long as the HDG panel. The HDG panel also shows some red rust. However, the scribe still seems to be protected in both systems. After cleaning, there are white corrosion products around the scribe in the case of the Zn23Al0.3Si system. They could not be removed in the acid. The presence of these products is interpreted as being indicative of a very high electrochemical activity of the Zn-Al topcoat. In the HDG system such tenacious products are not seen.

[00266] **Polarization Curves**

[00267] From potentiodynamic polarization curves in an electrolyte the initial corrosion rate of the metal is measured in that medium. The

electrochemical activity of the surface is measured. In addition to the corrosion current i_{corr}, which is converted to the corrosion rate in mpy (mm per year), the corrosion potential E_{corr} is measured. The lower the E_{corr}, the more active the metal surface is. Zinc surfaces in salt solutions, as are used here, typically have an E_{corr} slightly lower than -1 volt. Aluminum surfaces have a lower E_{corr}, provided they are not passivated. In salt solutions Al will not easily passivate, as the Cl^- ion depassivates it. Table 3 gives the E_{corr} and mpy values measured for HDG, Zn5Al and Zn23Al0.3Si. The values for delta-galvanized HDG, which is normally completely alloyed due to the high galvanizing temperature, are also measured. Figure 11 shows polarization curves for the Zn23Al0.3Si alloy and for HDG. There is no evidence for passivation of any of the alloys in this solution and the general shape of the curve for Zn23Al0.3Si is very similar to that of standard HDG. All other curves, e.g., for Zn5Al, are also similar to those of Figure 11.

[00268] The E_{corr} values shown in the Table do not vary significantly. They all are very close to the value for pure zinc and the variability between runs of the same material is about 20 mV. The differences between the i_{corr} values are significant, however. They show that HDG has a higher corrosion (dissolution) rate than the other systems. Zn5Al is a factor of 1½-2 lower than HDG, but Zn23Al0.3Si is a factor of 5 lower than HDG and a factor of 3 lower than Zn5Al. The corrosion rate of delta-galvanized HDG, if fully alloyed, is similar to that of Zn5Al and a factor of 1½-2 lower than regular HDG .

TABLE 3. Ecorr and mpy* values in aerated 3.5 wt.-% NaCl for HDG, Zn5Al and Zn23Al0.3Si coatings**

Coating	Ecorr, volts	Corrosion Rate, mpy
HDG	-1.030	60.6
delta-HDG	-1.020	37 - 70***
Zn5Al	-1.040	36.7
Zn23Al0.3Si	-1.020	13.3

* mils (25 µm) per year

** averaged for 5 samples

*** depending on whether complete alloying had occurred; these tests are performed with thin panels which does not fully alloy in the center; the higher value is obtained with the unalloyed regions

[00269] The overall corrosion results demonstrate that the Zn23Al0.3Si system has outstanding cathodic protection properties, despite the high Al content and despite the lower reactivity to form white rust, as compared with conventional HDG. They further seem to indicate that where cathodic protection is needed, e.g., around a defect area, the electrochemical activity of the coating increases. It can also be concluded that the Zn23Al0.3Si alloy is electrochemically just as reactive as the standard HDG, but the rate of zinc consumption in a corrosive environment is much lower, so the coating will last longer. It should be noted that these ratios, 1 : 3 : 5, are similar to the ratios found in the weight loss measurements for these alloys.

[00270] **Hardness**

[00271] The hardness of the two layers of the system, as measured by a micro-hardness tester in a cross section are listed in Table 4, which also shows the hardness of a bath sample and typical values obtained from the literature for the η, ξ, δ and Γ alloys in HDG when measured on the same scale (Vickers). It is seen that the interfacial reaction layer is very hard, even harder than the Γ layer in regular HDG. It increases with the silicon content in the bath and, therefore, silicon incorporated in this layer. The drag-out layer is softer, but still has a hardness value higher than that of the outermost layer in HDG, which is the η layer, consisting of almost pure zinc. Thus, these results show that the Zn23Al0.3Si system is hard and probably wear-resistant, but still ductile. The table also shows the very high hardness values for an additional layer that is only observed after very long dipping times. Its identity is not yet known, but it could be $Fe_{2-x}Al_5Si_x$, where x is nearly equal to 1, as the total coating thickness does not increase after long dipping times. Hence a transformation such as $Fe_2Al_5 + Si \rightarrow FeSiAl_5$ seems likely.

TABLE 4. Micro-Vickers Hardness of various alloys

Alloy	Micro-Vickers Hardness, HV
Mild Steel	159
η layer of HDG	70
ζ layer of HDG	179
δ layer of HDG	244
Γ layer of HDG	250
Zn23Al0.3Si, drag-out layer	105
Zn23Al0.3Si, reaction layer	380-400 and 700-900*
Zn23Al0.3Si bath sample	85
Steel	140-160

* depends on the dipping time; after very long dipping times, e.g., >10 min., a new layer with much higher hardness is observed under the Fe2Al5-x-yZnxSiy layer; its composition is not known, but it is probably a layer with a higher Si content, e.g., FeSiAl5.

[00272] Bath Properties

[00273] Some observations regarding dross formation and stability of the Zn23Al0.3Si bath composition are:

1. The silicon level of the bath decreases very slowly with a number of dips. For example, after dipping 26 panels of 75×105 mm in the 30-kg bath held at 575-600°C, with dipping times of 5-8 min., the Si level had dropped from 0.38 wt.-% to 0.36 wt.-%. That is not more than 5% of the original Si content. This is considered a very positive result as the silicon level is easily maintained by adding some of the Zn23Al2Si master alloy. Further, as explained earlier, the silicon level is not very critical and is somewhere between 0.2 and 0.7 wt.-%.

2. Bath iron content, bottom dross and top dross are monitored with time.

It is found that the equilibrium iron content of the bath is of the order of 0.02 wt.-%. It does not increase with time.

3. It is also observed that bottom dross – in regular galvanizing insoluble iron-zinc alloys with higher melting points than zinc – is not formed in the Zn23Al0.3Si bath. As far as top dross (ash) formation is concerned, it is observed that noticeable top dross only formed after replenishing the bath with the two master alloys. Analysis of that dross shows a higher iron content, e.g., 0.8 wt.-%. The Si and Al contents of the top dross are identical to that of the bath. The amount of top dross does not increase with time..

[00274] **Example 1.**

[00275] Materials. The bath was made up by melting ingots of the master alloys Zn23Al and Zn23Al1Si. They were melted in such ratios that a bath analysis of 23 wt.-% Al and 0.2-0.7 wt.-% Si was obtained. The steels that were tested consisted of a variety of cold-rolled and hot-rolled carbon steel panels of 75×105 mm and 2.5 mm thickness. A series of steels with known Si and P levels was also galvanized.

[00276] Cleaning and Fluxing. All samples were cleaned in an alkaline degreaser for 10 min. at 70°C, followed by a 20-25 min. dip at 25°C in an acid cleaner. The panels were then and fluxed in a flux based on the conventional zinc-ammonium chloride flux modified for use with Al-containing zinc baths. Immediately after cleaning, the steels were fluxed 2 min. at 55°C and then dried at 100°C for 10-15 min. They were galvanized within 15 min. after fluxing.

[00277] Bath Preparation and Dipping. A 30-kg laboratory silicon carbide crucible was mostly used. Larger samples were immersed into a 500-kg crucible. Insertion speed was 60 cm/min. The immersion time, bath temperature, the silicon level of the bath and the steel quality were varied. The fluxing process, the immersion speed, the bath composition other than the Si level were not varied.

[00278] Bath Analysis. The bath was analyzed for Zn, Al, Si and Fe levels at regular intervals.

[00279] SEM/EDX of Cross Sections. Polished and etched cross sections of the coating were analyzed by SEM/EDX. Of some samples s.e. images of the surface were also taken.

[00280] Corrosion Testing. Panels were exposed to a salt fog (ASTM B-117). The criterion for failure was the appearances of traces of red rust. When red rust appeared, the panels were cleaned as per ASTM G1 in order to remove the white rust. In other exposures, the weight loss in the test was monitored and compared with that of conventional hot-dip galvanized panels and with panels dipped into a Zn5Al bath of 450°C. In another set of experiments the galvanized panels were first bent by 180° and then exposed in the B-117 test with the purpose to verify the ductility of the Zn23Al0.3Si coating. Red rust was expected to appear first on the bend. HDG and Zn5Al coatings were used as controls.

[00281] Hardness Measurements. The hardness of the coatings was estimated in cross sections using a Leco 400 micro-hardness device.

[00282] Rhesca Experiments. Preliminary experiments were carried out with sheets of IF steel and cold-rolled steel (CRS), which were dipped for a few seconds into a bath of Zn23Al0.03Si held at 550°C. These sheets were not fluxed but, after pickling and scrubbing, they were deoxidized at 520°C in a N2/H2 mixture for 30 s. The Si level of the bath was lowered in order to stimulate the formation of the intermetallic layer at the interface.

[00283] RESULTS AND DISCUSSION

[00284] Experiments with various fluxes. Our modified flux, based on zinc ammonium chloride, developed for the Zn5Al alloy, worked well and formed outburst-free coatings in the range of 550-600°C. Thus, this flux was used in all experiments discussed in this paper. The treatment time and temperature were kept constant.

[00285] Coating Structure. The surface of the coatings produced at 0.3% Si was smooth and did not show clear spangles. s.e. images of the surface showed either an interdendritic phase system or two distinct phases (figure not shown). This two-phase system was typically found for thinner panels that were cooled rapidly or galvanized at lower temperatures. The primary (or alpha) phase is the eutectoid composition (Zn/Al = 77/23) Al-rich phase,

that is formed upon cooling below 406°C. The coarser secondary phase is formed from the remaining liquid.

[00286] The samples produced show a coating exhibiting two continuous layers. The thin layer at the metal-coating interface is Fe2-x-yAl5ZnxSiy. This layer has a thickness of 5-10 μm. The top layer has approximately the bath composition, so it is termed the drag-out layer. This layer exhibits a distinct lamellar structure. Thus, it must be composed of the two phases into which the eutectoid composition decomposes, initially Zn/Al = 31/68 and 99/1 (figure not shown), but, depending on the cooling rate experienced, the Al-rich phase can become richer in Al. One sample shows a sample in which regions with the eutectoid composition are embedded in another phase. This is an Al-rich interdendritic phase which has not been completely converted.

[00287] Si was distributed throughout the entire coating. However, its level in the Fe2-x-yAl5ZnxSiy phase was higher than the overall bath composition. Thus, Si in the bath stabilizes the Fe2-x-yAl5ZnxSiy layer, as the entire coating is now devoid of Fe-Zn outbursts. As a result, the coating is of a simple structure, viz., that of a solidified drag-out layer on top of a Fe-Al reaction layer. The structure of the Fe2-x-yAl5ZnxSiy layer is not much dependent on the cooling rate, whereas the structure of the drag-out layer is dependent.

[00288] Effect of Dipping Conditions. The effect of dipping time, dipping temperature and silicon level of the bath was investigated. The following observations were made.

[00289] Effect of dipping time. At 575°C and 0.18 wt.-% Si the thickness of the interfacial layer increased parabolically with time, whereas that of the outer layer remained constant.

[00290] Effect of dipping temperature. At 0.4 wt.-% Si the thickness of the inner layer increased approximately linearly with the temperature for 1 min. dipping time. The range of 550°C to 600°C was investigated here. The thickness of the outer layer remained constant until 575°C and then decreased.

[00291] Effect of bath levels of silicon. So far, the range of 0.18 to 0.75 wt.-% has been investigated. Below 0.18 wt.-% the coating formation was uncontrolled due to the outbursting effect. In the range of 0.18 to about 0.7 wt.-%, the thickness of both inner and outer layer layer did not change significantly for several temperatures in the range of 550-600°C and for all dipping times. At 0.75 wt.-%, the thickness of the inner layer decreased sharply, but did not disappear completely. The thickness of the outer layer did not vary with silicon level.

[00292] Effect of Si Level of the Steel. A set of steels with various Si and P levels were dipped at 575°C for 5 min. in a bath with 0.4 wt.-% Si. The following conclusions can be drawn from the results.

[00293] The total coating thickness was 25-30 μm. There is no effect of the silicon or phosphorus content on the total layer thickness. The drag-out layer was similar in all cases and fairly continuous with occasional evidence for the Al-rich interdendritic layer mentioned earlier. This layer does not depend on the steel composition. The silicon content of the interfacial reaction layer is in all cases higher than that of the bath, viz., up to about 8 wt.-%. Again, there is no clear trend with the steel composition.

[00294] In the steels with either very high Si (0.35 wt.-%) or P (0.052 wt.-%) content, the interfacial reaction layer was no longer continuous. Although the thickness remains the same, there were regions where that layer was broken up or missing.

[00295] These results show that the Sandelin effect associated with general galvanizing does not play a role when the Zn23Al0.3Si bath is used. Many qualities of steel can be effectively coated without effect on coating thickness or performance.

[00296] Corrosion Properties Salt spray resistance. The panels are tested after treatment of regular HDG and Zn23Al0.3Si panels after exposure in the B-117 test. The HDG was removed after 350 hours, the Zn23Al0.3Si after 2000 hours. The HDG panel had formed red rust., the new alloy had not. Panels of Zn5Al (not shown) lasted about 600 hours in this test. Thus, the Zn5Al coatings are a factor of 2 better than HDG, the Zn23Al0.3Si coating is a factor 6-7 better. It should be noted that the coating thickness of the

HDG panels was 75 μm, whereas that on both the Zn5Al and Zn23Al0.3Si was not more than 25-30 μm.

[00297] Weight loss measurements. The weight loss in the salt spray test was measured quantitatively in another test involving HDG, Zn5Al and Zn23Al0.3Si. The results are shown in Table 1. On a daily basis these weight loss ratios are 1 : 3 : 9. These ratios are similar to the red rust appearance data and they demonstrate that it is not only the interfacial iron-aluminide layer but the Zn-Al drag-out layer as well that contributes to the outstanding corrosion resistance of high-Al-containing coatings.

[00298] Bend test. In another test, panels of the three coating systems were bent in a vise and then exposed in the salt spray chamber again. The purpose was to verify whether the Zn23Al0.3Si system is ductile. The criterion in this test was the appearance of red rust in the bend, i.e., the region of the highest tensile stresses. The HDG panels were exposed for only 3 days, as red rust had already become apparent. The Zn5Al and Zn23Al0.3Si panels were exposed for 24 days. It was observed that the HDG panel showed a large amounts of white rust and had also formed red rust in the bend area. The Zn5Al panel began to break down as it showed local spots of red rust. The Zn23Al0.3Si panel showed less white rust than the other systems and not a single spot of red rust. Thus, it can be concluded that this coating can withstand severe deformations better than HDG and Zn5Al.

[00299] Hardness. The hardness of the two layers of the system are listed in Table 2, which also shows the hardness of a bath sample. It is seen that the interfacial reaction layer is very hard, even harder than the Γ layer in regular HDG. It increases with the silicon content in the bath and, therefore, silicon incorporated in this layer. The drag-out layer is softer, but still has a hardness value higher than that of HDG. Thus, these results show that the Zn23Al0.3Si system is hard but still ductile.

[00300] Bath Properties. The properties of the Zn23Al0.3Si bath have not yet been studied in great detail. However, some observations regarding dross formation and stability of the bath composition are worth mentioning here.

[00301] The silicon level of the bath decreased only very slowly with a number of dips. Bath iron content, bottom dross and top dross were monitored with

time. It was found that the equilibrium iron content of the bath was of the order of 0.02 wt.-%. It did not increase with time. It was also observed that bottom dross was not formed in the Zn23Al0.3Si bath. Hence, if clean master alloys are used, this Zn23Al0.3Si galvanizing process is a very clean process with practically no iron dissolution, no bottom dross and very low top dross (ash) formation.

[00302] Rhesca experiments. The IF steel was dipped for 5 s, the CRS was dipped for 20 s. It is seen that the IF steel had formed a layer of about 20-30 μm with a very thin but uniform intermetallic layer. The CRS sheet had formed a 60 μm layer with up to ¾ being the intermetallic layer. At shorter dipping times the layer was thinner, but still had appreciable amounts of the intermetallic layer. The intermetallic layers did not show outburst in these experiments. It is thus shown that by adjusting the Si level of the bath, layer can be obtained which are very similar to those obtained in the batch process.

[00303] That the intermetallic layer controls the corrosion performance was again confirmed by the observation that the 180° IF steel sheet began to show red rust at the bend and in a scribe after 450 hours of salt spray exposure. Regular HDG showed large amounts of red rust all over after 168 hours. The bent CRS sheet did not show red rust at the bend or in a scribe after 1200 hours of exposure.

[00304] Results with production material. A number of 30-cm long tubes, square tubes, and C channels to which two thick end plates had been welded, were galvanized in order to mimic production materials. The tubular parts of the samples were heavily rusted. The process was no changed, except that pickling was done longer than for the small laboratory samples. The results were generally good. The leveling effect of the drag-out layer and the formation of a uniform interfacial layer of 7 μm thickness can be seen. The total layer thickness is 20-40 μm.

[00305] SUMMARY AND CONCLUSIONS

[00306] The typical dipping conditions of this alloy are 2-5 minutes at 550°C Both cold-rolled and hot-rolled steels can be galvanized. The bath contains only one additive other than zinc and aluminum, viz., silicon. This additive

suppresses the outbursting effect effectively if used in the range of 0.2-0.7 wt.-%. The properties of the new alloy coating are independent of the silicon content of the steel. The thickness of the coating is about 25-30 μm, i.e., half that of currently used galvanized coatings. The coating has a simple structure consisting of an interfacial iron-aluminum layer (mainly Fe2Al5 or Fe2-x-yAl5ZnxSiy) at the steel coating interface and a drag-out layer of approximately the bath composition. This bath does not form bottom dross. Steel sheets can be galvanized in the same bath if the Si level is lowered to 0.03%. The coating thickness and structure is then similar to that of the batch process. The coatings thank their extraordinary corrosion resistance to the intermetallic Fe2Al5 layer, not to the drag-out ZnAl layer.

[00307] In addition, information regarding procedural or other details supplementary to those set forth herein is described in cited references specifically incorporated herein by reference.

CLAIMS:

1. A method of galvanizing with a molten zinc-alloy comprising immersing a ferrous material to be coated in a flux bath in an independent vessel thereby creating a flux coated ferrous material and thereafter immersing the flux coated ferrous material in a molten zinc-aluminum alloy bath in a separate vessel to be coated with a zinc-aluminum alloy layer thereby creating a coating on the ferrous material, wherein the molten zinc-aluminum alloy is a zinc alloy of a high aluminum content comprising 10%-40% by weight of aluminum, at least 0.2% by weight of silicon, and the balance being zinc and optionally comprising one or more additional elements selected from the group consisting of magnesium and a rare earth element.

2. The method according to claim 1, wherein the molten zinc-aluminum alloy bath consists essentially of an aluminum-zinc alloy containing 20%-25% by weight of Al and 0.2%-0.9% by weight of Si and the remainder is zinc.

3. The method according to claim 1, wherein the molten zinc-aluminum alloy bath consists essentially of an aluminum-zinc alloy containing 22%-24% by weight of Al and 0.2%-0.7% by weight of Si and the remainder is zinc.

4. The method according to claim 1, wherein the material to be coated is immersed in the molten zinc-aluminum alloy bath for at least 1 minute.

5. The method according to claim 1, wherein the temperature of the molten zinc-aluminum alloy bath in a separate dip galvanizing vessel is from about 500 to about 650°C.

6. The method according to claim 2, wherein the temperature of the molten zinc-aluminum alloy bath is from about 510 to about 625°C.

7. The method according to claim 2, wherein the coating has an average thickness of about 10-60 μm.

8. The method according to claim 1, wherein the ferrous material is selected from the group consisting of interstitial-free (IF), hot-rolled, low carbon, ultra-low carbon, titanium, chromium and stainless steels.

9. The method according to claim 1, wherein the flux is ALUFLUX.

10. The method according to claim 1, wherein the flux bath comprises 20 to 90 wt

% of zinc chloride and 10 to 20 wt % of at least one metal chloride.

11. The method according to claim 10, wherein the metal chloride is selected from the group consisting of an alkali metal chloride and an alkaline earth metal chloride.

12. The method according to claim 11, wherein the metal chloride is ammonium chloride.

13. The method according to claim 1, wherein the flux bath comprises from about 10 to 40 weight % zinc chloride, about 1 to 15 weight % ammonium chloride, about 1 to 15 weight % of an alkali metal chloride, a surfactant and an acidic component such that the flux has a final pH of about 1.5 or less.

14. The method according to claim 1, wherein the flux bath comprises from about 15 to 40 weight % zinc chloride, about 1 to 10 weight % ammonium chloride, about 1 to 6 weight % of an alkali metal chloride, a nonionic surfactant and an acidic component such that the flux has a final pH of about 1.5 or less.

15. The method according to claim 1, wherein the flux bath comprises from about 15 to 40 weight % zinc chloride, about 1 to 10 weight % ammonium chloride, about 1 to 6 weight % of an alkali metal chloride, about 0.01 to 0.5 weight % of a nonionic surfactant, and an acidic component such that the flux has a pH of about 1.5 or less.

16. The method according to claim 14, wherein the flux bath further comprises about 1 to 4 weight % ferric chloride.

17. The method according to claim 14, wherein the alkali metal chloride comprises one or more of the group consisting of lithium chloride, potassium chloride and sodium chloride.

18. The method according to claim 14, wherein the flux bath further comprises about 0.1 to 0.2 weight % of an inhibitor containing an amino derivative.

19. The method according to claim 18, wherein the amino derivative comprises an aliphatic alkyl amine.

20. The method according to claim 19, wherein the alkyl amine comprises one or more of the group consisting of C_1 to C_{12} alkyl amines.

21. The method according to claim 20, wherein the alkyl amine is selected from

one or more of hexamethylenediamine tetra, hexapotassium hexamethylenediamine and alkyldimethyl quaternary ammonium nitrate.

22. The method according to claim 18, wherein the amino derivative comprises an alkyltrimethyl ammonium chloride.

23. The method according to claim 14, wherein the nonionic surfactant contains polyoxyethylenated straight-chain alcohols with a hydrophile-lipophile balance (HLB) of less than 11.

24. The method according to claim 1, wherein the flux bath comprises from about 15 to 40 weight % zinc chloride, about 1 to 10 weight % ammonium chloride, about 1 to 4 weight % ferric chloride, about 1 to 6 weight % of an alkali metal chloride, about 0.02 to 0.1 weight % of a nonionic surfactant, about 0.01 to 0.2 weight % of an inhibitor containing an amino derivative, and an acidic component so that the flux has a pH of about 1.5 or less.

25. The method according to claim 1, wherein the flux bath comprises from about 15 to 40 weight % zinc chloride, about 1 to 10 weight % ammonium chloride, about 1 to 6 weight % of an alkali metal chloride, about 0.02 to 0.1 weight % of a surfactant, and an acidic component so that the flux has a pH of about 1.5 or less.

26. The method according to claim 1, wherein the flux bath comprises from about 15 to 40 weight % zinc chloride, about 1 to 10 weight % ammonium chloride, about 1 to 4 weight % ferric chloride, about 1 to 6 weight % of an alkali metal chloride, about 0.02 to 0.1 weight % of a nonionic surfactant, about 0.1 to 0.2 weight % of an inhibitor containing an amino derivative, and an acidic component so that the flux has a pH of about 1.5 or less.

27. An ferrous metal article provided with a coating according to the method of claim 13.

28. The method according to claim 13, characterized in that it comprises between 200 and 700 g/l of the flux, preferably between 350 and 550 g/l, most preferably between 500 and 550 g/l.

29. The method according to claim 13, wherein the flux bath is maintained at a temperature of about 20 to about 90°C.

30. The method according to claim 13, wherein the flux bath is maintained at a temperature of about 50 and 90°C.

31. The method according to claim 13, wherein the flux bath further comprises additional additives comprising one or more of iron, nickel, cobalt, boron, carbon, chromium, molybdenum, manganese, tungsten, and silicon.

32. The method according to claim 13, wherein the flux bath comprises a non-ionic surfactant in a concentration of between 0.01 to 2 vol. %.

33. The method according to claim 13, wherein the surface of the ferrous material is first cleaned of an oxide film by degreasing and pickling.

34. A molten zinc-aluminum alloy of high-aluminum content hot dip galvanizing bath consisting essentially of 22-24 wt.% of Al; about 0.18 to about 0.75 wt.% Si; with the rest comprising Zn, wherein the temperature of the molten zinc-aluminum alloy bath is from about 510 to about 625°C.

35. The hot dip galvanizing bath of claim 34 comprising about 0.2 to about 0.7 wt % Si.

36. The hot dip galvanizing bath of claim 34 further comprising 0.001-0.6% by weight nickel.

37. The hot dip galvanizing bath of claim 34 further comprising 0.001-0.6% by weight vanadium.

38. A fluxless method for the hot dip galvanization of a ferrous metal article comprising dipping the article in a molten zinc-aluminum alloy bath to form a metal coating thereon, wherein the molten zinc-aluminum alloy is a zinc alloy of a high aluminum content comprising 10-40 wt% aluminum, 0.01%-0.9% by weight of silicon, and the balance being zinc and optionally comprising one, or two or more additional elements selected from the group consisting of magnesium and a rare earth element.

39. The method according to claim 38, wherein the molten zinc-aluminum alloy bath consists essentially of an aluminum-zinc alloy containing 20%-25% by weight of Al and 0.03%-0.7% by weight of Si and the remainder is zinc.

40. The method according to claim 38, wherein the molten zinc-aluminum alloy bath consists essentially of an aluminum-zinc alloy containing 22%-24% by weight of Al and 0.03%-0.5% by weight of Si and the remainder is zinc.

41. The method according to claim 38, wherein the temperature of the molten zinc-aluminum alloy bath in a separate dip galvanizing vessel is at least

500°C.

42. The method according to claim 38, wherein the temperature of the molten zinc-aluminum alloy bath is from about 510 to about 625°C.

43. The method according to claim 38, wherein the coating is applied in a continuous hot-dip galvanizing process.

44. The method according to claim 38, wherein the material to be coated is immersed in the molten zinc-aluminum alloy bath for at least 1 second.

45. The method according to claim 38, wherein the material to be coated is immersed in the molten zinc-aluminum alloy bath in a continuous process for at least 1 second.

46. The method according to claim 38, wherein the method further comprises the steps: (a) heating the article to a temperature of at least 400°C and (b) reacting the article in a reducing atmosphere; prior to dipping the article in the molten zinc-aluminum alloy bath.

47. The method according to claim 46, wherein the method further comprises one or more of the steps: (a) degreasing the article in a degreasing bath; (b) rinsing the article; (c) pickling the article; and (d) rinsing the article; prior to dipping the article in the molten zinc-aluminum alloy bath.

48. The method according to claim 47 wherein the degreasing step comprises dipping the ferrous article for about 5 to about 60 minutes in an alkaline solution containing sodium hydroxide and sodium orthosilicate in a weight ratio of about 1:1, and a concentration of 10 to 15%, at a temperature of about 60°C to about 80°C.

49. The hot dip galvanizing bath of claim 48 comprising about 20 to about 25 wt % Al.

50. The hot dip galvanizing bath of claim 49 comprising about 0.2 to about 0.7 wt % Si.

51. An ferrous metal article provided with a coating according to the method of claim 38.

52. A process for hot dip-coating a ferrous material with a molten zinc alloy of a high aluminum content according to a one-stage metal alloy coating method using a flux, wherein the method consists essentially of removing an oxide

layer which is present on a ferrous material surface, coating the ferrous material surface with a chloride flux solution consisting essentially of (a) at least one chloride selected from the group consisting of zinc chloride and aluminum chloride and (b) at least one chloride selected form the group consisting of potassium chloride, lithium chloride and sodium chloride, thereby forming a coating film of a chloride flux on the ferrous material, and dipping the ferrous material in a molten zinc-aluminum alloy bath to form a metal coating thereon, wherein the molten zinc-aluminum alloy is a zinc alloy of a high aluminum content comprising 10-40 wt% aluminum, 0.2%-0.9% by weight of silicon, and the balance being zinc and optionally comprising one, or two or more additional elements selected from the group consisting of magnesium and a rare earth element.

53. The method according to claim 52, wherein the molten zinc-aluminum alloy bath consists essentially of an aluminum-zinc alloy containing 10%-40% by weight of Al, 0.2%-0.7% by weight of Si and the remainder is zinc.

54. The method according to claim 52, wherein the molten zinc-aluminum alloy bath consists essentially of an aluminum-zinc alloy containing 20%-25% by weight of Al and 0.2%-0.5% by weight of Si and the remainder is zinc.

55. A ferrous metal article provided with a coating according to the method of claim 52.

56. A process for continuous galvanizing of metal strips, tubes and wires with a molten zinc alloy of a high aluminum content according to a one-stage metal alloy coating method, wherein the method consists essentially of substantially removing an oxide layer which is present on a ferrous material surface and dipping the ferrous material in a molten zinc-aluminum alloy bath to form a metal coating thereon, wherein the molten zinc-aluminum alloy is a zinc alloy of a high aluminum content comprising 10-40 wt% aluminum, 0.2%-0.9% by weight of silicon, and the balance being zinc and optionally comprising one or more additional elements selected from the group consisting of magnesium and a rare earth element.

57. The method according to claim 56, wherein the method further comprises the step of coating the ferrous material surface with a chloride flux solution consisting essentially of (a) at least one chloride selected from the group consisting of zinc chloride and aluminum chloride and (b) at least one chloride

selected form the group consisting of potassium chloride, lithium chloride and sodium chloride, thereby forming a coating film of a chloride flux on the ferrous material, before coating in the molten zinc-aluminum alloy bath.

58. The method according to claim 56, wherein the oxide layer is substantially removed by the treatment selected from the group consisting of treating with a flux, heating to at least 500° in a reducing atmosphere or both.

59. The method according to claim 56, wherein the molten zinc-aluminum alloy bath consists essentially of an aluminum-zinc alloy containing 10%-40% by weight of Al, 0.2%-0.7% by weight of Si and the remainder is zinc.

60. The method according to claim 56, wherein the molten zinc-aluminum alloy bath consists essentially of an aluminum-zinc alloy containing 20%-25% by weight of Al and 0.2%-0.5% by weight of Si and the remainder is zinc.

61. The method according to claim 58, wherein the strip, tube or wire is heated in a furnace with a reducing atmosphere comprising N_2 gas containing at least 0.5% of H_2 gas.

62. The method according to claim 56, wherein the wire, strip or tube is heated to near the temperature of the zinc bath while at the same time surface oxides are substantially removed by reactions with the reducing gas.

63. The method according to claim 56, wherein the wire, strip or tube is heated to within 200°C of the temperature of the zinc bath.

64. The method according to claim 56, wherein the wire, strip or tube is heated to within 50°C of the temperature of the zinc bath.

65. An ferrous metal article provided with a coating according to the method of claim 56.

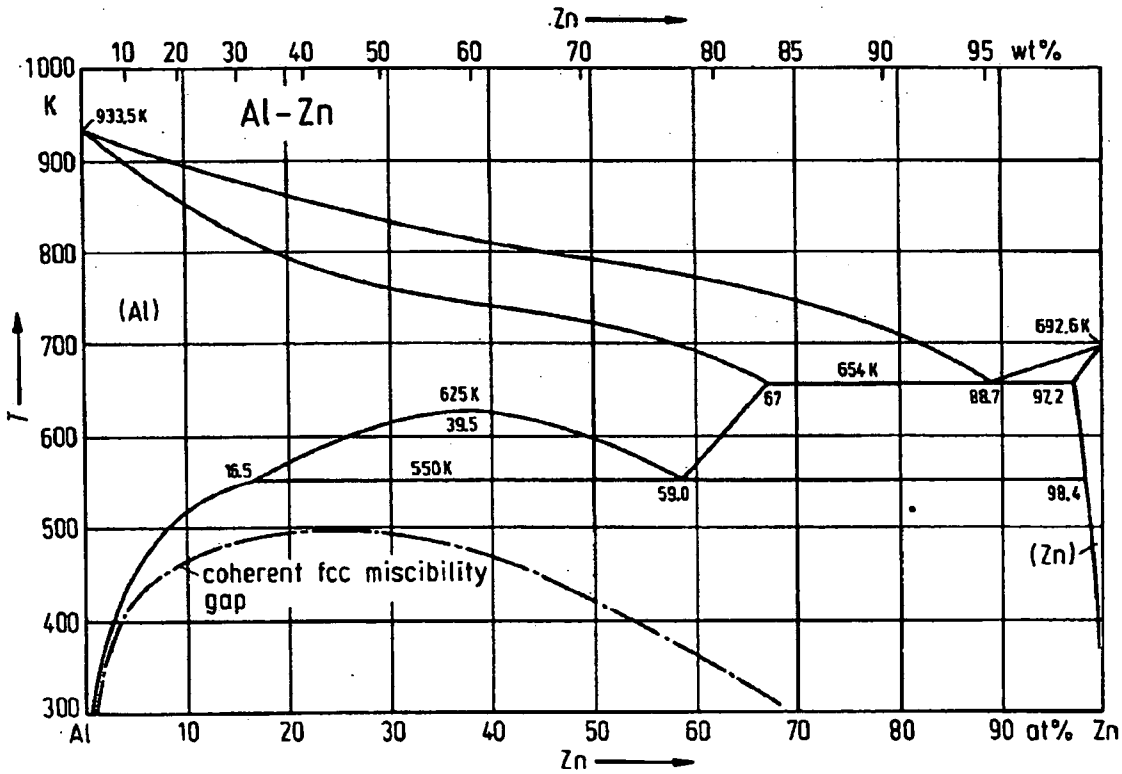


Figure 1. Zinc-aluminum binary phase diagram

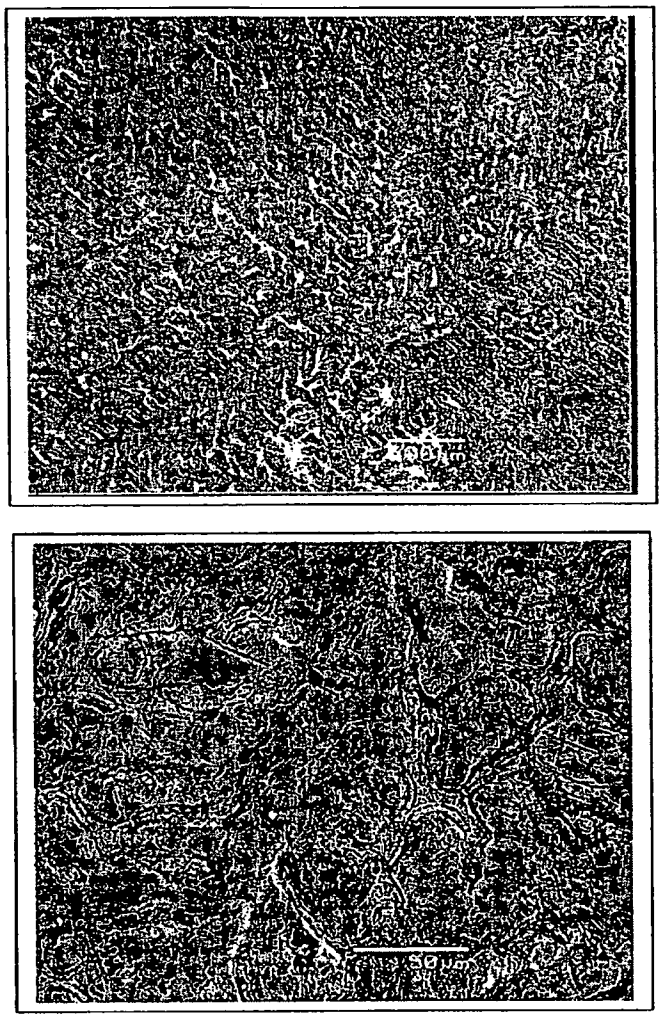
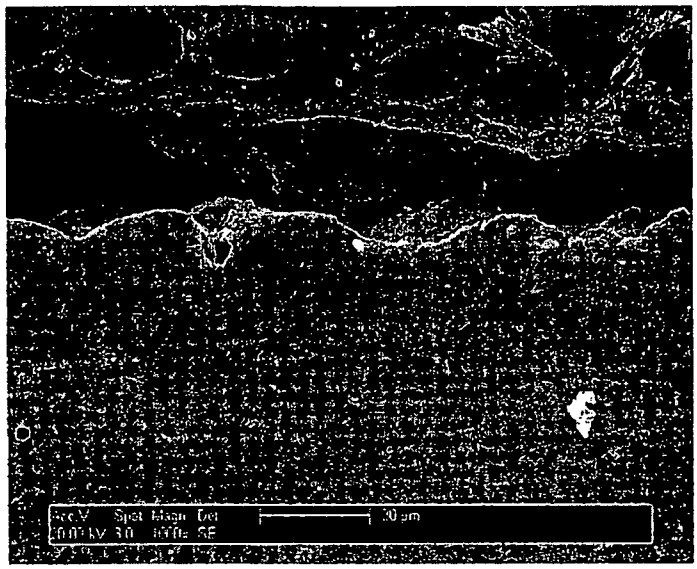
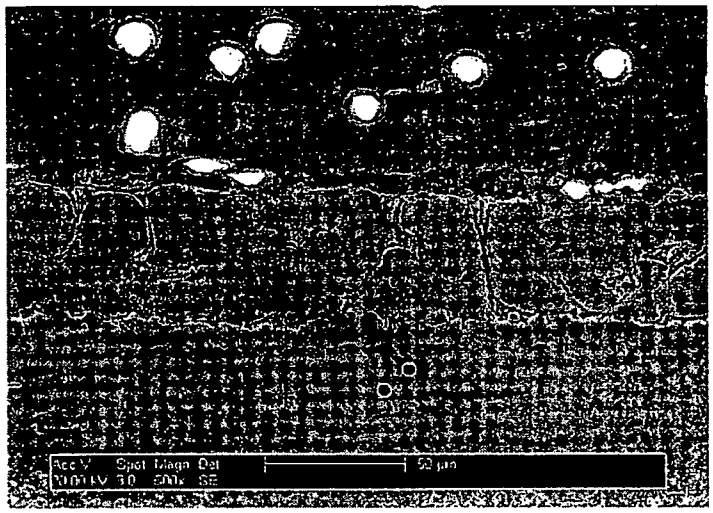


Figure 2. Secondary electron images of surface of Zn23Al0.3Si alloy on steel dipped for 2 min. at 575°C; Si content of bath 0.18 wt.-%; top: 75X; bottom, 1000X

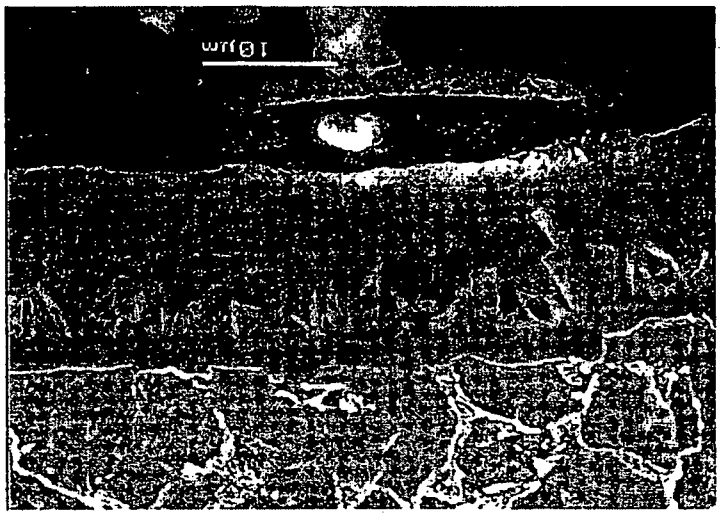


(a)

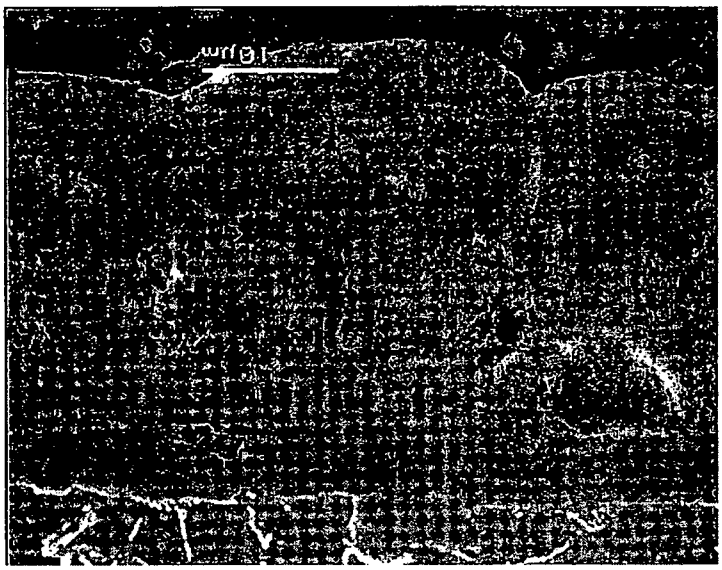


(b)

Figure 3. Secondary electron image of cross sections of Zn23Al0.3Si coating; (a) thick steel sample dipped for 5 min. at 575°C in bath with 0.75 wt.-% Si; (b) thinner steel plate dipped for 5 min at 550°C in bath with 0.4 wt.-% Si

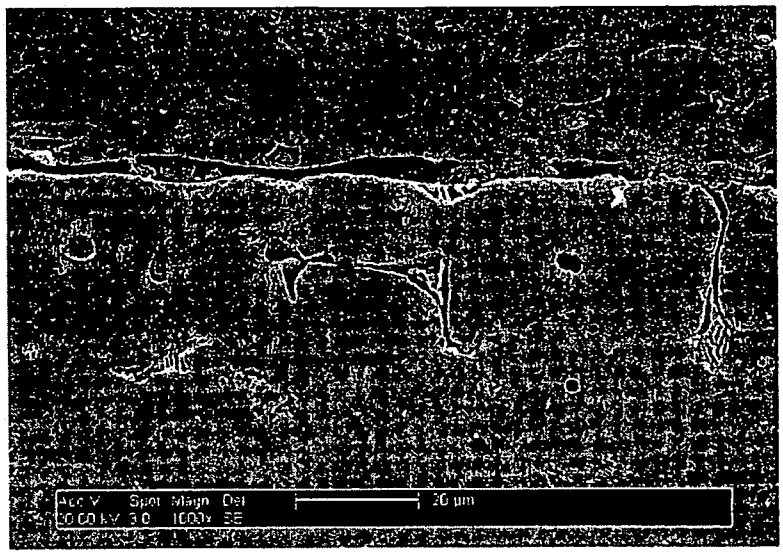


(a)

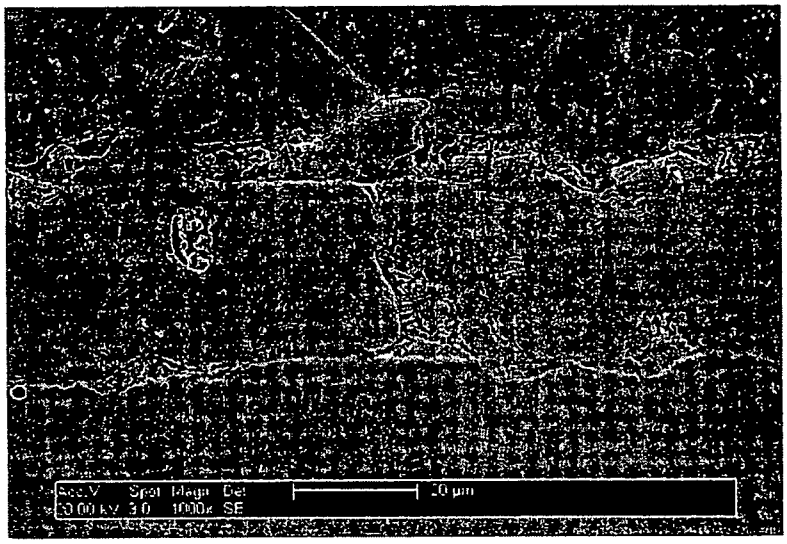


(b)

Figure 4. Secondary electron images of Zn23Al0.3Si coatings on steel; (a) dipped for 1 min. in bath with 0.18 wt.-% Si at 575°C; (b) dipped for 10 min. in same bath

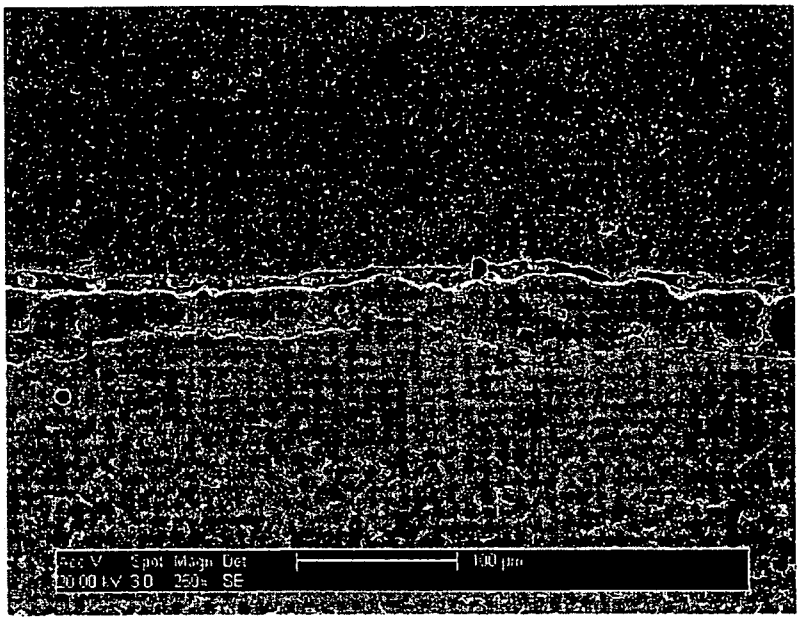


(a)



(b)

Figure 5. Secondary electron images of Zn23Al0.3Si coatings on steel dipped for 5 min. at 575°C in bath with 0.5 wt.-% Si; (a) steel no. 2 of Table 1(low Si; low P); (b) steel no. 7 of Table 1 (high Si; low P); the Fe_2Al_5 layer is locally missing

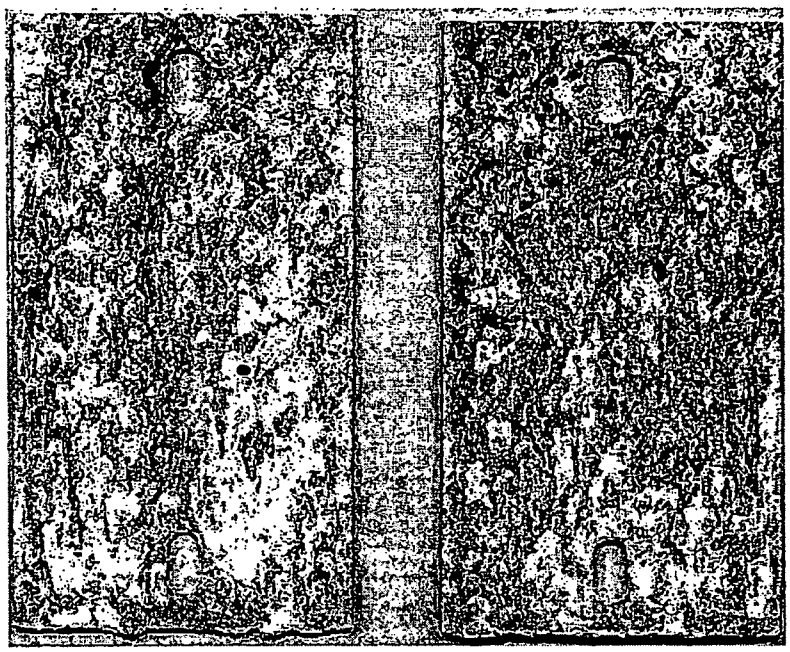


(a)

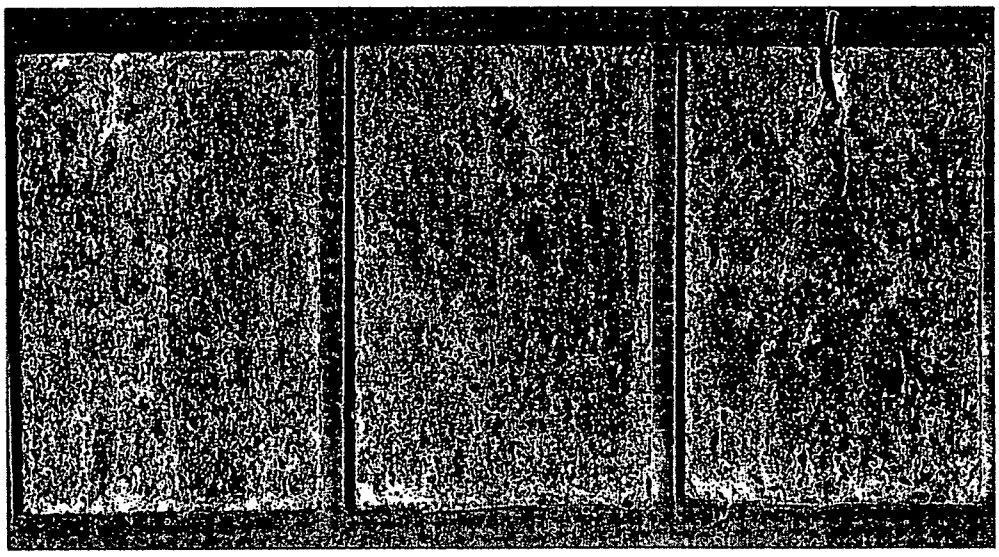


(b)

Figure 6. Secondary electron images of Zn23Al0.3Si coatings on steel no. 10 of Table 1 dipped for 5 min. at 575°C in bath with 0.5 wt.-% Si; (a) low magnification; (b) higher magnification; the formation of the Fe_2Al_5 layer is locally interrupted

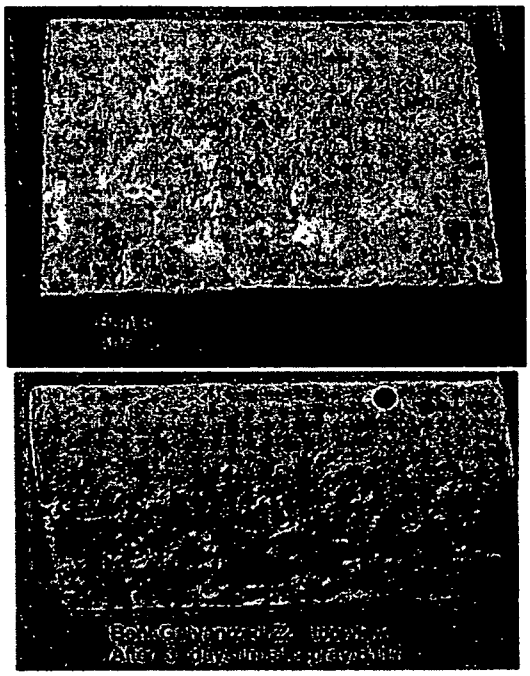


(a)



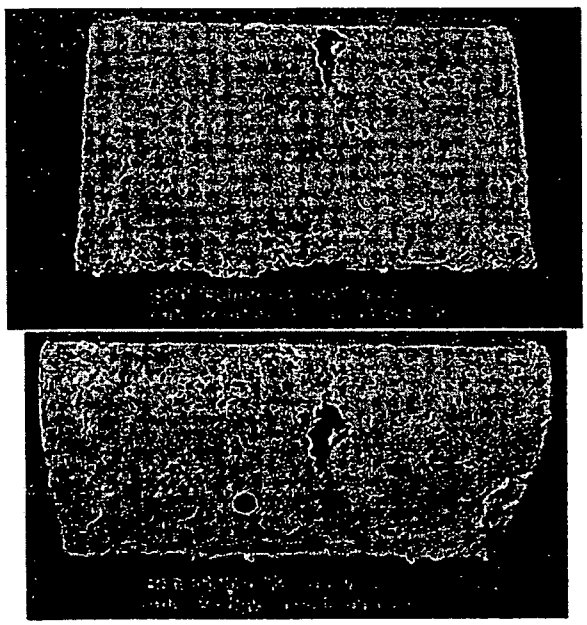
(b)

Figure 7. Galvanized panels after exposure in the B-117 salt spray test; (a) conventional HDG, exposed for 350 hours, showing red rust; (b) Zn23Al0.3Si-coated steel after exposure for 2000 hours; one of the panels showed one spot of red rust; the surface had darkened considerably



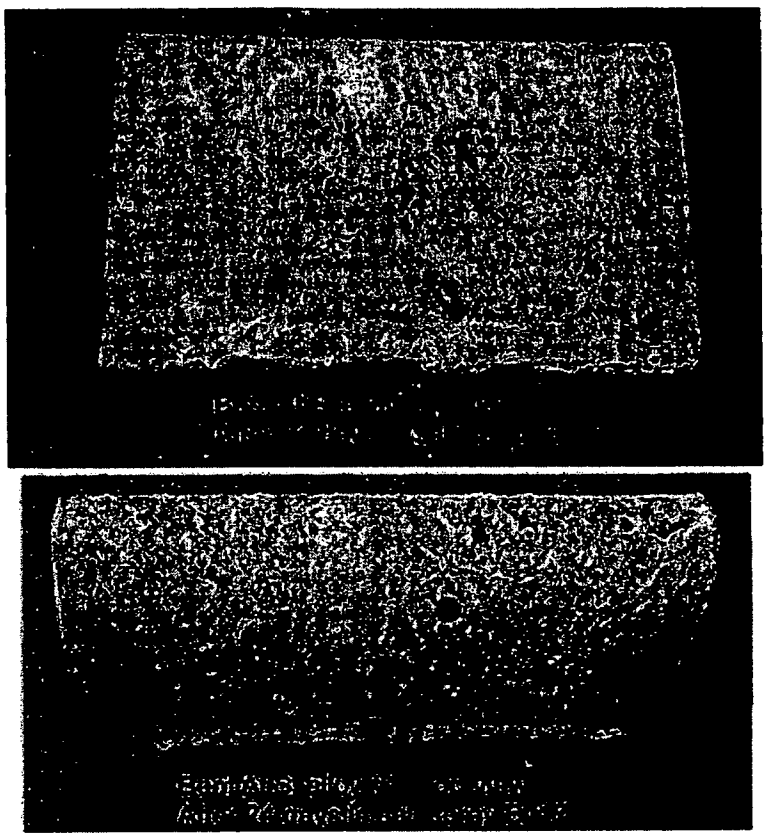
Bent
HDG

(a)



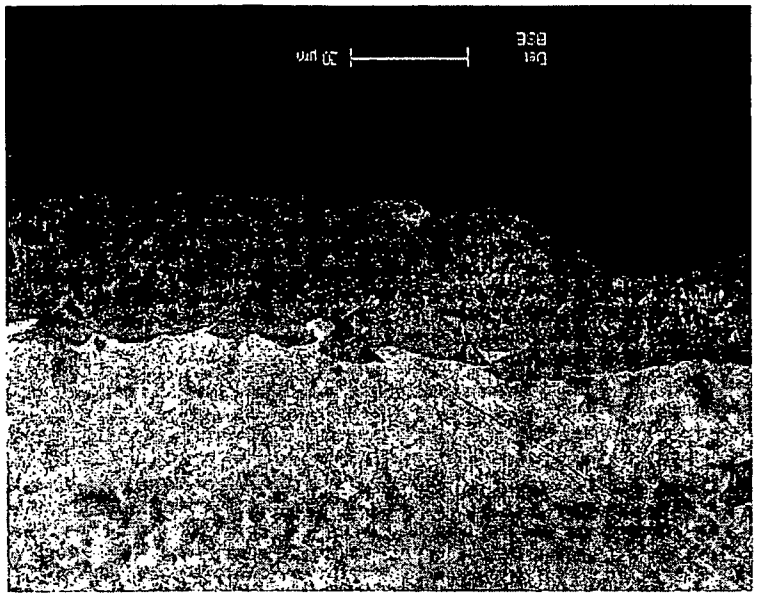
Bent
Zn5Al

(b)



(c)

Figure 8. Galvanized panels after bending over 180° followed by exposure in the B-117 salt spray test; (a) conventional HDG exposed for 3 days; red rust is observed in the bent area; (b) Zn5Al-coated steel exposed for 24 days; red rust is beginning to form; (c) Zn23Al0.3Si-coated steel exposed for 24 days; no red rust is observed



(a)

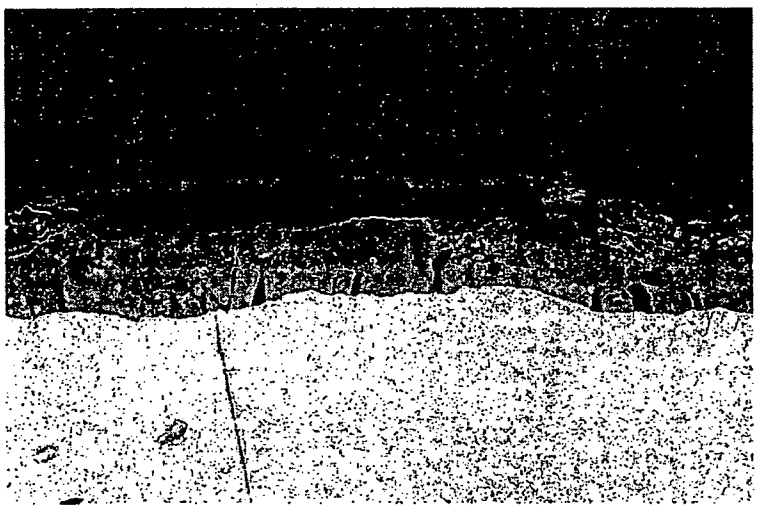
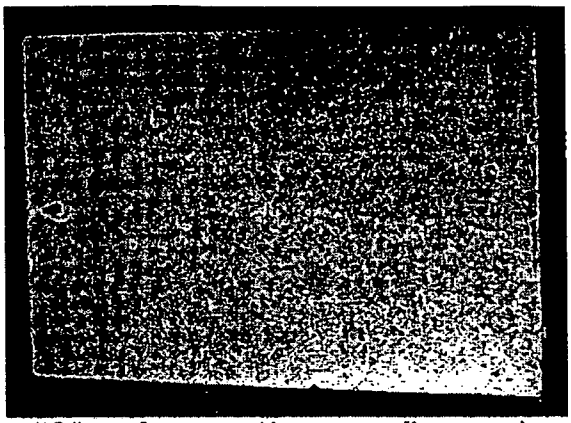
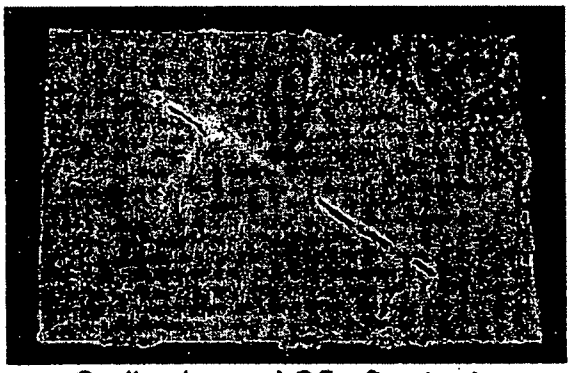


Figure 9. Secondary electron images of Zn23Al0.3Si-coated steel panels after bending over 180°; (a) side of the panel that was in compression; (b) side of the panel that was in tension; this was the side viewed in Figure 8; there are no cracks in the ZnAl layer; the Fe_2Al_5 layer has cracked in tension



"S" series panel - no scribe mark

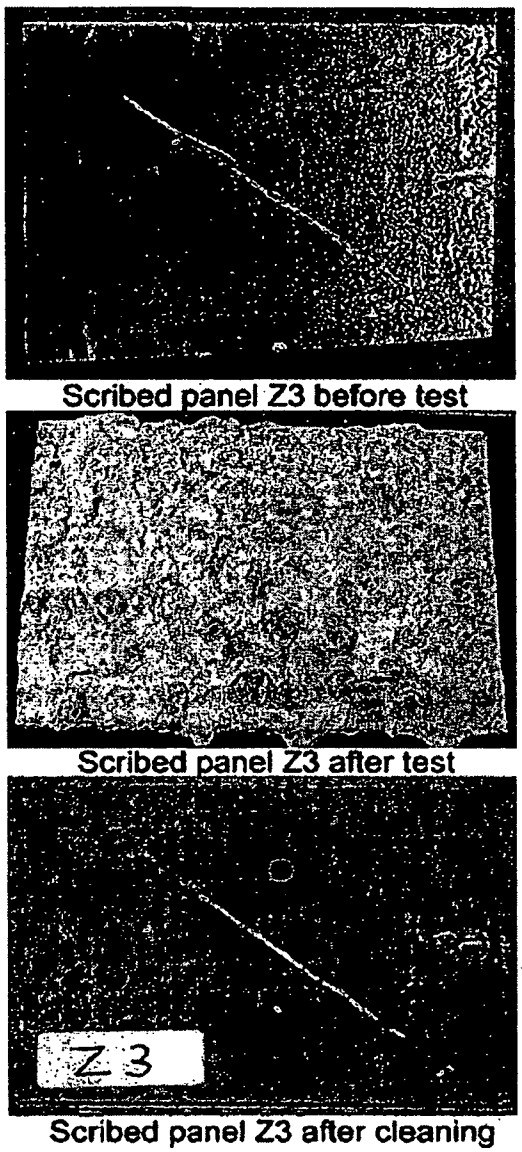


Scribed panel S5 after test



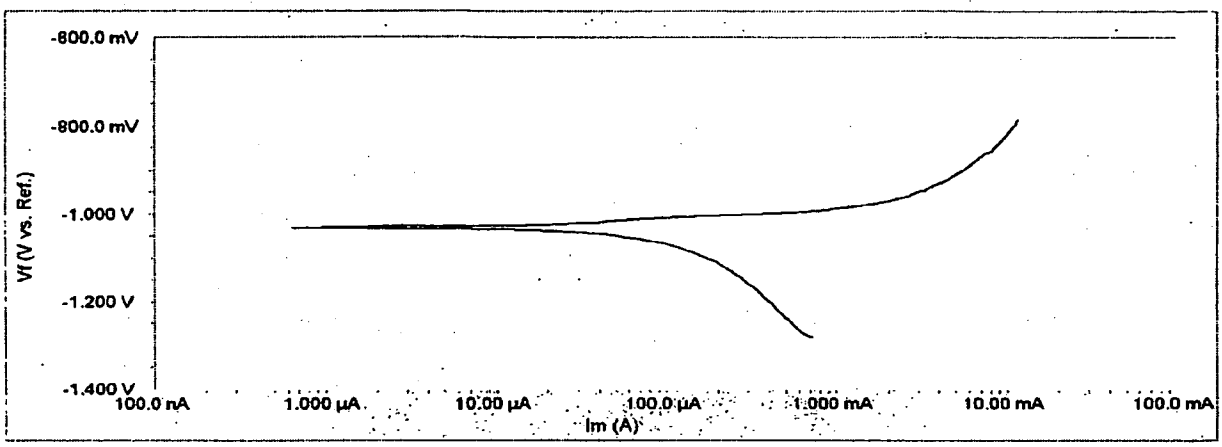
Scribed panel S5 after cleaning

(a)

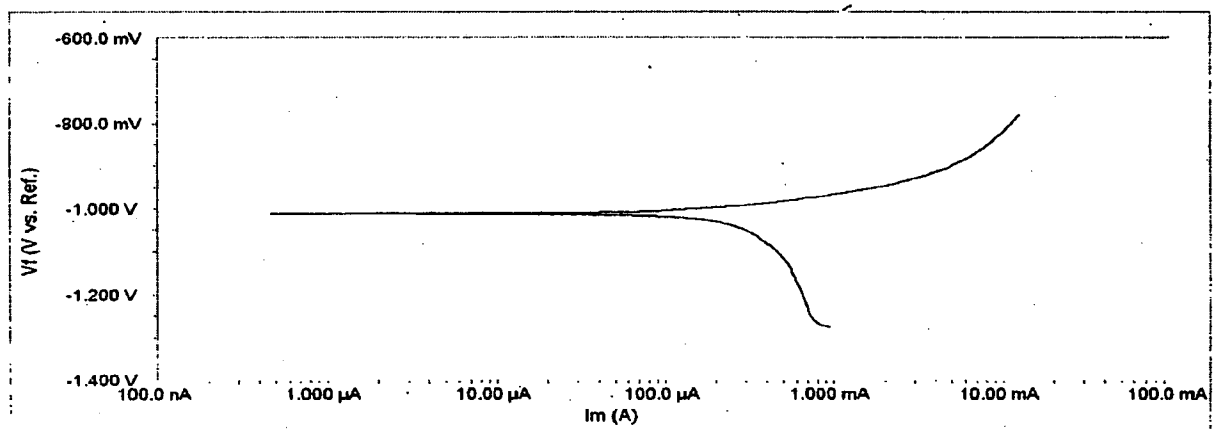


(b)

Figure 10. Scribed galvanized panels before and after exposure in the B-117 salt spray test and after cleaning to remove the white rust; (a) Zn23Al03.Si- coated panels after 24 days of exposure showing protection of the scribe; (b) conventional HDG panels after 14 days showing larger amounts of white rust and formation of red rust; the scribe was still protected



(a)



(b)

Figure 11. Typical potentiodynamic polarization curve of (a) Zn23Al0.3Si-coated steel in aerated 3.5 wt.-% NaCl, showing a very active surface, absence of passivation and a corrosion potential similar to that of conventional HDG, whose curve is shown in (b)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 07/13562

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C23C 2/02 (2007.01)
USPC - 427/433
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC - 427/433

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC -427/320, 329, 406; 148/23 (text search - see terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST (PGPB,USPT,USOC,EPAB,JPAB); Google
Search Terms: galvanizing, molten, zinc alloy, ferrous, material, flux, coated, silicon, chloride, aluminum

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 5,853,806 A (HIGUCHI et al.) 29 December 1998 (29.12.1998) entire document, especially col 4, 5, 6, 7, 9, 10, 21	1-9 and 34-35 ---------- 10-33 and 36-65
Y	US 5,437,738 A (GERENROT et al.) 1 August 1995 (01.08.1995) col 4, ln 59-60; col 5, ln 11-35; col 7, ln 21-44	10-33 and 52-65
Y	US 6,458,425 B2 (FERRERO et al.) 1 October 2002 (01.10.2002) col 2, ln 56-65	36-37
Y	US 4,444,814 A (FLINCHRUM et al.) 24 April 1984 (24.04.1984) col 1, ln 20-27; col 2, ln 35; col 4, ln 14-16; col 6, ln 67 to col 7, ln 7; col 10, ln 3-4	38-51
Y	US 6,200,636 B1 (VAN OOIJ et al.) 13 March 2001 (13.03.2001) col 5, ln 24-30	48-50
A	LOPEZ. "Effects of Nonionic Surfactants on the Interactions of Different Nanoparticle Materials on Glass Surfaces" 30 March 2005 (30.03.2005) pages 16 and 76	23
A	"Material Safety Data Sheet Aluflux 1000 Experimental" 20 November 1992 (20.11.1992) ENTIRE DOCUMENT	9

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 October 2007 (08.10.2007)	07 NOV 2007

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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