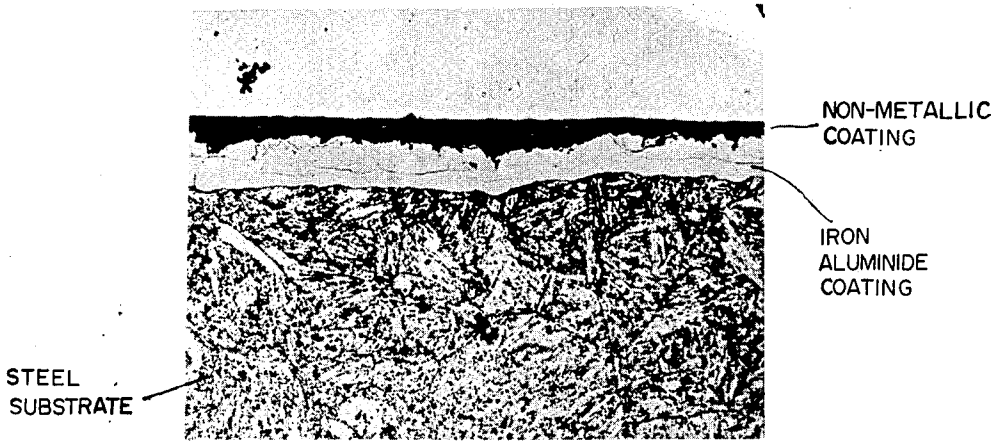
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CORROSION RESISTANT COATING SYSTEM

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CORROSION RESISTANT COATING SYSTEM

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ABSTRACT OF THE DISCLOSURE

Ferrous metal articles are provided having improved resistance to corrosion in highly saline and/or marine atmospheres, the articles being characterized by a protective duplex coating comprised of a sacrificial thermally aluminized ferrous metal surface in a combination with a special barrier type non-metallic overcoat. One method of providing the foregoing system is to apply an adherent layer from a liquid of a soluble silicate salt or compound onto a thermally aluminized layer, the silicate layer being preferably thereafter cured. In a preferred embodiment, a conversion coating is applied to the silicate layer and cured *in situ* to further enhance the resistance to corrosion.

This is a division of application Ser. No. 143,842, filed May 17, 1971, now U.S. Pat. No. 3,729,295.

This invention relates to the protection of ferrous metal articles from corrosion in highly saline and/or marine atmospheres by employing a protective duplex coating compound of a sacrificial thermally aluminized ferrous metal surface in combination with a special barrier-type non-metallic overcoat.

FIELD OF THE INVENTION

Jet and gas turbine engine compressor components are subject to corrosion in highly saline atmosphere at the air intake end of the engine and also to direct impact of abrasive particulate matter, such as coral dust. Additionally, the compressor blades are subjected to tremendous mechanical stresses from centrifugal forces, thermal shock, vibration and other sources of stresses. Thus, corrosion can accelerate catastrophic failure, since pits and other corrosion defects can act as stress raisers.

High strength ferrous alloys are employed in the construction of compressor blades and other aircraft engine components (e.g. Society of Automotive Engineers alloy designation AMS 5508, AMS 5616, AMS 6304 and others) but, because of their low resistance to saline corrosion, they are generally subjected to a protective surface treatment. One, in particular, is the provision of an aluminum-base diffusion coating on the ferrous substrate by pack-aluminizing at coating temperatures ranging up to 1000° F. and preferably not higher so as to avoid undesired crystallographic or metallurgical changes in the substrate during coating, which might have an adverse or undesired effect on the mechanical properties of the parts. Such coatings have provided advantageous oxidation and erosion resistance and have minimized the production of pulverous corrosion products and have been very useful in extending the operating life of jet engine components.

However, while such treatments have helped measurably to improve the corrosion life of the ferrous article, the trend has been towards the further improvement of the reliability of jet engine systems, particularly with the advent of more stringent requirements to reduce the downtime for maintenance and overhauling.

A surface treatment has now been discovered which provides optimum resistance to corrosion for prolonged periods of time by providing a novel duplex coating system. As far as is known, this novel system was not available prior to this invention.

OBJECTS OF THE INVENTION

It is thus the object of this invention to provide a protective duplex coating for ferrous articles.

Another object is to provide a method for further enhancing the corrosion resistance of ferrous metal substrates by applying thereto a protective duplex coating comprising a sacrificial thermally aluminized coating in combination with a special barrier type non-metallic overcoat.

These and other objects will more clearly appear when taken in conjunction with the following description, the appended claims and the accompanying drawing which depicts at 500 times magnification the novel protective duplex coating of the invention.

STATEMENT OF THE INVENTION

This invention is based on the discovery that the corrosion resistance of ferrous metal articles can be unexpectedly enhanced by providing the ferrous article with a protective duplex coating system comprising thermally aluminizing the ferrous substrate and then applying thereto a highly adherent barrier type non-metallic overcoat containing a silicate salt or compound as an essential ingredient.

It is believed that the markedly improved resistance to corrosion is due to a synergistic effect between the thermally aluminized coating which is characterized by an iron aluminide intermetallic and the non-metallic overcoat. It is known according to U.S. Pat. No. 2,529,206, that alkali metal silicates applied to the surface of ferrous articles will enhance the resistance of the ferrous article to corrosion. However, this treatment *per se* does not provide the desirable corrosion resistance necessary for the aggravated conditions which prevail in jet engines operating in corrosive saline environments.

Tests have indicated that the intermetallic iron aluminide produced by the pack aluminizing of ferrous articles in a bed containing essentially alumina, some aluminum powder and a small but effective amount of a halide, e.g. $AlCl_3$, and the like, is characterized by the ability to absorb readily a silicate liquid, such as an aqueous solution of sodium silicate. It is believed that the high affinity of the aluminized coating for the silicate is associated with the physical-chemical character of the aluminized surface arising out of the method of growth of the aluminide. Observations have indicated that the iron aluminide formed at the surface is characterized by an exceptionally high surface area, high degree of chemical cleanliness and chemical activity. It is believed that the foregoing characteristics provide for synergistic effects which lead to unexpected improved results. The expression "thermally aluminized surface" is meant to cover the thermal diffusion of aluminum in a ferrous surface in which iron aluminide is formed at the surface.

One embodiment of the invention resides in a method which comprises applying to the thermally aluminized surface of the article a solution of a soluble silicate salt at a temperature ranging up to about 100° C., for example, about 70° C. to 95° C. (about 160° F. to 200 F.), removing excess liquid from the surface, such as by blowing it off with air, to form a uniform layer of said silicate salt, and then drying the layer on said surface.

While the aluminized surface in and of itself exhibits some resistance to saline corrosion, a typical salt spray test shows that sacrificial products form after approximately 15 hours of testing, whereas times in excess of 200

hours have been repeately obtained when the aluminized surface is coated with a uniform silicate layer. This result appears to confirm the synergistic effects which accrue when the silicate contacts the iron aluminide at the interface.

A wide range of sodium silicate solutions can be employed in carrying out the invention. For example, the solutions can be prepared from solutions of 50 to 100% concentrations of $Na_2O \cdot 3.22SiO_2$. Various other sodium silicates can be employed to prepare solutions such as Baumé 40, 45, 47 and 50. Potassium silicate may be similarly employed. Lithium silicate and also organic silicates can be used, such as ethyl silicate.

DETAILS OF THE INVENTION

A preferred solution for producing a uniform precoat on the intermetallic iron aluminide substrate is on containing by weight about 0.05 to 2% SiO_2 equivalent, for example, a soluble silicate in the form of $Na_2O \cdot 3.22SiO_2$. The temperature of the substrate during application should preferably range from about 70 C. to 95° C.

A preferred method for applying the silicate solution pre-coat at the foregoing concentration comprises immersing the thermally aluminized ferrous article (e.g. a compressor blade) in a tank maintained at a temperature of about 70° C. to 95° C. with sufficient time in the bath to bring the article to temperature and assure absorption of the solution into the aluminized surface. The excess liquid is then blown off with air and the part allowed to dry. It is immersed again for a brief period for a time sufficient to allow the article to be covered with liquid, after which it is removed, blown off with air and air dried. The steps may be repeated until the desired thickness is obtained. It has been found that when using the air-drying technique, only short dips in the tank need be employed to ensure a continuous build-up of the silicate layer. Leaving the part in the bath too long can result in the layer being redissolved in the solution. To assure wettability of the coating on the intermetallic substrate, an anionic surfactant or wetting agent may be employed, for example, an anionic phosphate surfactant, such as Triton QS–30 (manufactured by Rohm & Haas).

An alternate method which yields a more stable silicate coating resides in applying a succession of layers as described hereinabove followed by curing in an oven. Infra-red or forced air heated ovens may be employed in the temperature range of about 150° C. to 430° C. (about 300° F. to 805° F.) with enhanced corrosion protection. The silicate coating applied by any of the methods described herein will produce a uniform layer with a thickness of approximately 0.0001 inch (0.1 mil) while avoiding as far as is possible areas of excess silicate on the surface. A preferred method is to apply at least one pre-coat from a dilute silicate bath containing 0.05% to 2% by weight of SiO_2 equivalent by a series of dipping, drying and curing steps followed by at least one spray coating of silicate from a more concentrated solution containing about 2.5% to 17.5% (e.g. 6.8%) by weight of SiO_2 equivalent.

The advantage of curing the silicate coating which allows multiple layers to be formed is that the cured coating can withstand ten oxidation-corrosion cycles comprising heating the coated substrate to 1000° F. (about 538° C.) for 1 hour followed by 5 hours of salt spray testing, for foregoing test being repeated for ten cycles. In contrast, the intermetallic layer on a stainless steel substrate without the silicate coating provides protection for only 3 cycles, with pitting occurring in the stainless steel substrate. Applications of the silicate coating followed by curing at about 400° F. (205° C.) have yielded high degrees of protection and, in many cases, very little sacrificial products have been observed after 10 cycles of heating to 1000° F. (538° C.) followed by the salt spray test. The foregoing tests are helpful as controls in assuring the quality of the silicate coating before the next coating treatment is applied.

The corrosion resistance of the intermetallic layer is further enhanced by applying a conversion coating to the cured silicate layer. The conversion coating in turn may be covered by a silicate layer. The conversion may be applied by spraying, using commercially available reciprocating guns. Following the application of the conversion coating, the silicate solution containing 6.8% by weight equivalent of SiO_2 and containing about 0.002% by weight of an anionic phosphate surfactant may optionally be sprayed over the conversion coating having a surface temperature not exceeding about 150° F. (65° C.) followed by curing at temperatures from about 300° F. (150° C.) to about 805° F. (430° C.) for 10 minutes in an infra-red furnace. Another method of covering the conversion coating is to dip the article in a hot solution of about 180° F. to 200° F. (82° C. to 93° C.), using a sodium silicate concentration of about 0.9% to 2.4% by weight of SiO_2 equivalent with a 0.002% addition of an anionic phosphate surfactant.

The article is immersed in the bath and allowed to come to temperature and excess liquid removed rapidly by means of an air gun. It is then immersed again and immediately pulled out of the solution and air dried. A third application is made in the same manner. It is important that excess liquid be removed from the part to avoid foaming during curing. The purpose of repeated immersion and drying is to assure uniform coating of the surface. As stated above, the curing is preferably carried out at about 800° F. in an infra-red furnace.

A simple production procedure which has been found successful for applying uniform layers of silicate is as follows:

Compressor blades of AMS 5616 steel are subjected to 4 cycles of treatment in the solution by supporting the blades on a rack which is immersed in the solution and immediately withdrawn. The liquid is allowed to drain for approximately 15 seconds, after which it is immersed again and withdrawn. Following the second dip, an annular air collar (air pressure at about 70 p.s.i.) is disposed about the rack of blades to blow off the excess liquid. This is achieved by raising the rack through and above the air collar to allow the parts to drain, the air valve opened, and the rack then caused to be lowered through the collar. This group of steps constitutes one cycle. Four cycles are employed to produce the desired silicate layer. If necessary, an air gun can be used to remove excess liquid from the root of the blades. After the fourth cycle, the blades are dried free of moisture by, for example, blowing with air. The temperature at which the silicate layers are applied may range from about 160° F. (70° C.) to 200° F. (90° C.). Following completion of the four cycles, the coating on the dried blade is then cured at about 800° F. (425° C.) in an infra-red oven.

As stated hereinabove, apparently the synergistic effect is achieved between the iron aluminide in the aluminized surface and the applied silicate coating such that the tendency for the aluminized surface to corrode sacrificially is markedly inhibited, wherein the life of the sacrificial coating is unexpectedly extended for longer periods of time in saline environments than heretofore obtained with the aluminized surface.

However, as stated hereinabove, the life of the silicated sacrificial aluminized coating is further enhanced by the application of a conversion coating from a solution in substanially the manner in which the silicate coating is applied. An aqueous conversion coating solution which is preferred may range by weight from about 5% to 30% phosphoric acid (preferably 10% to 30%), about 0.0235% to 3% aluminum, about 3% to 8% chromic acid (CrO_3), about 0.75% to 6% magnesium, and the

balance essentially water. A formation found particularly preferred in producing the solution is as follows:

	Wt. percent
Phosphoric acid	15.0
Aluminum powder	0.225
Chromic acid (CrO_3)	5.0
Magnesium turnings	1.5
Non-anionic surfactant comprising a condensation product of ethylene oxide with an alkylphenol (Triton X–100 by Rohm & Haas)	0.1
Water	78.175
	100.00

The aluminum and magnesium are dissolved in the solution by virtue of the free acid present.

In conversion coating silicated blades, both sides of the blades are sprayed simultaneously, then dried and cured in the oven which heats the blade surface to a temperature of about 800° F. (427° C.). The blades are then cooled prior to the next application of the coating. The steps of spraying, baking and cooling constitute one spray cycle. Three spray cycles are normally used in applying the conversion coating.

The application of the conversion coating as described above results in a smooth uniform surface layer which provides oxidation-corrosion protection without the need for supplementary surface finishing. A build-up of approximately 0.1 mil can be obtained by employing a plurality of silicate and conversion coating applications.

As illustrative of the invention, the following example is given.

EXAMPLE 1

A group of compressor blades is first aluminized by preparing an aluminizing pack comprised of 800 lbs. of —60+140 mesh aluminum powder blended with 200 lbs. of Al_2O_3, also —60+140 mesh size. To the 1000 lb. mixture is added 30 lbs. of dry $AlCl_3$ under a humidity preferably not exceeding 45%.

The pack is mixed in a vibrating blender from aobut 5 to 10 minutes. If the charge is a fresh charge, it is subjected to burn-out at 795–825° F. (425° C. to 440° C.) for 36 hours. However, where a charge has already been used, burn-out is not required. The pack is placed in a dry condition in a retort with the compressor blades of AMS 5616 steel to be treated, the blades being completely embedded in the pack. The cover is sealed to the retort body with multiple layers of aluminum foil in the form of a gasket sufficient to prevent air from getting in but to allow out-gassing of gaseous by-products.

The retort is placed in an oven at ambient temperature and the temperature allowed to rise to the desired coating temperature by the application of heat. As the temperature rises, it goes through an endothermic arrest at about 350° F. (176° C.) due to vaporization of $AlCl_3$ and then allowed to reach a range of about 795° F. to 825° F. (425° C. to 440° C.) and the retort maintained at substantially that temperature range for about 36 hours. Upon completion of the heating cycle, the retort is removed from the even and allowed to cool approximately to 400° F. (205° C.), after which it is placed in a dry environment for cooling to ambient temperature.

The cooled retort is then placed in a humidity control cabinet, the cover removed and the compressor blades taken out of the cementation pack. The blades are cleaned of adhering coating compound by blowing with dry air and immersed in water to remove fine dust and other residues to provide a very clean aluminum deposit containing an iron aluminide intermetallic compound, such as $FeAl_3$. The aluminized surface, like other thermally diffused aluminum coatings, has some sacrificial properties in that it will corrode in preference to the ferrous substrate in saline environments and, therefore, provide some measure of protection of the ferrous substrate against corrosion. A characteristic of thermally diffused alminum coatings is that it readily absorbs dilute liquid silicate solutions due to its microporosity and apparently synergistically reacts with the silicate to provide an adherent protective precoat.

Following the production of the aluminum-coated blades, the blades are racked and the rack immersed in a tank containing an aqueous sodium silicate solution containing by weight about 0.1% to 2% SiO_2 equivalent maintained at a temperature ranging from about 160° F. to 200° F. (70° C. to 95° C.). The bath also contained a small but effective amount of an anionic phosphate surfactant. The blades are immersed for a time sufficient to reach the temperature of the bath and then withdrawn, the excess liquid being blown off with air and the blades allowed to then dry. The process is repeated a number of times until a desired thickness is obtained, e.g. 0.05 mil. Several blades coated in this manner exhibited improved resistance to corrosion. The resistance to corrosion was even further improved by subjecting the silicated thermally aluminized blades to an oven cure at a temperature within the range of about 300° F. (150° C.) to 800° F. (430° C.).

As conducive to a better understanding of the invention, a series of oxidation-salt spray corrosion tests was conducted on AMS 5616 steel compressor blades, some with and without a thermally aluminized surface and some with and without various forms of non-metallic overcoats. Thus, the blade test specimens in the series outside the invention include (A) the bare steel substrate; (B) the bare steel substrate with a cured sodium silicate pre-coat; (C) the bare steel substrate with alternate cured layers of sodium silicate and a cured conversion coating; (D) the bare steel surface with only a cured conversion coating; (E) a bare steel specimen with a cured conversion coat containing about 0.1% by weight of SiO_2 equivalent (as sodium silicate); (F) the steel substrate with only a thermally aluminized surface containing iron aluminide; and (G) the steel substrate with the thermally aluminized surface and with a cured overcoat of the conversion coating. The series within the invention included (1) the steel substrate with the thermally aluminized surface with a cured overcoat of sodium silicate; (2) the steel substrate with the thermally aluminized surface which in turn has the overcoat as in (C); and (3) the steel substrate with the thermally aluminized surface covered with an overcoat of the conversion coating containing about 0.1% by weight of SiO_2 equivalent as sodium silicate.

The corrosion testing cycle comprised heating the blade specimens for 1 hour at 900° F. followed cooling and then subjecting the cooled specimen to 5 hours of salt spray in accordance with ASTM B117–64. The foregoing, which is considered one cycle, is repeated generally 10 times or more to obtain an evaluation of the relative quality of each of the coating systems. The results and details of the tests are given in the following table:

OXIDATION-COMPRESSION TESTS OF AMS 5616 STEEL COMPRESSOR BLADES WITH AND WITHOUT THE DUPLEX COATING

Test No.	Preparation	Percent of surface corroded
A	None—bare steel surface	100% of surface corroded after first cycle.
B	Bare steel surface with pre-coat of sodium silicate from a ½ to 1 vol. percent solution (about 0.15 to 0.3 wt. percent SiO_2 equivalent) and then cured.	25% of surface corroded after 2 cycles and 100% corrosion after 4th cycle.
C	Bare steel surface coated as follows: (a) pre-coat of sodium silicate from ½ to 1 vol. percent solution (about 0.15 to 0.3 wt. percent SiO_2) and cured; (b) spray coat with 25 vol. percent sodium silicate solution (7.3% by wt. SiO_2) and cured; (c) spray coat with conversion coat [1] and cured; (d) spray coat with 25 vol. percent sodium silicate (7.3 wt. percent SiO_2) and cured.	25% of surface corroded after 5th cycle, over 50% corroded after 8th cycle and 85% corroded after the 12th cycle.

TABLE—Continued

Test No.	Preparation	Percent of surface corroded
D	Bare steel surface with conversion coat. [1]	Over 45% of surface corroded after 3d cycle and over 80% corroded after 8th cycle.
E	Bare steel surface with conversion coat [1] containing 0.1% by wt. of SiO_2 equivalent as sodium silicate.	45% of surface corroded after 3d cycle and over 90% corroded after 8th cycle.
F	Aluminized steel surface containing iron aluminide alone.	25% of surface corroded after 8th cycle, 55% after 10th cycle and 90% after 12th cycle.

[1] Conversion coating obtained from a solution containing by weight 15% phosphoric, 5% chromic acid, 0.225% dissolved aluminum, 1.5% dissolved magnesium. 0.1% of anionic phosphate surfacant, and the balance water (78.175%).

Test No.	Preparation	Percent of surface corroded
1	Aluminized steel surface as in F with overcoat of cured sodium silicate deposited from a solution of ½ to 1 vol. percent sodium silicate (based on 41.5 Baumé). This corresponds to 0.15 to 0.3 wt. percent SiO_2 equivalent.	Only 5% of surface corroded after the 8th cycle and 10% after the 12th cycle.
2	Aluminized steel surface as in F with overcoat as in C.	No surface corrosion after 8th cycle and only 1% surface corroded after 13th cycle.
3	Aluminized steel surface as in F with overcoat of conversion coating [1] containing 0.1 wt. percent SiO_2 equivalent as sodium silicate.	No surface corrosion after the 8th cycle, 10% after 10th cycle and 25% after 13th cycle.

[1] Conversion coating obtained from a sclution containing by weight 15% phosphoric, 5% chromic acid, 0.225% dissolved aluminum, 1.5% dissolved magensium, 0.1% anionic phosphate surfactant, and the balance water (78.175%).

A test (G) was conducted in which the aluminized surface was provided with the conversion coating given in the footnote of the above table. The results obtained after 13 cycles were inferior to Test Nos. 1, 2 and 3.

The curing of the silicate coatings was carried out at about 400° F. (205° C.) for about 10 minutes in an infra-red furnace while that of the conversion coating was carried out at about 800° F. (425° C.) in the infra-red furnace for approximately the same time period. As will be noted from the table, test specimens A to F (outside the invention) showed deterioration much sooner than specimens 1 to 3 (within the invention). It will be particularly noted that Test No. 1 (aluminized surface plus cured sodium silicate) exhibits nine times the improvement over Test No. F (aluminized only) after the eighth cycle on the amount of area corroded. As a further contrast, Test Nos. 1 and 2 showed very little corrosion after the 12th cycle.

As regards Test No. 2, reference is made to the accompanying drawing which depicts a micrograph illustrated at 500 times magnification showing the steel substrate with the iron aluminide coating characterized by surface microporosity and having strongly bonded thereto the non-metallic overcoat produced in accordance with Test No. 2.

The duplex coating system of Test No. 2 is particularly advantageous. In this system, the non-metallic overcoat is applied (as described in Test No. C) in a series of steps as follows: (1) The aluminized steel surface is provided with a pre-coat of sodium silicate applied by a series of dips in a solution containing by weight about 0.15% to 0.3% SiO_2 equivalent and then cured; (2) a spray coat of silicate is applied containing 25 vol. percent of sodium silicate (obtained from 41.5 Baumé solution) corresponding to 7.3 wt. percent of SiO_2 equivalent followed by curing; (3) the conversion coat is then sprayed onto the cured silicate layer; and (4) lastly, sodium silicate of about 25 vol. percent concentration (about 7.3 wt. percent SiO_2 equivalent) is sprayed over the conversion coat and thereafter cured. The sodium silicate solutions were prepared from Baumé 41.5 solutions.

When the silicate solution is employed as a dip (sodium silicate, potassium silicate and ethyl silicates), the concentration of the dip solution generally ranges by weight from about 0.05% to 2% SiO_2 equivalent. Where the silicate is employed as a sprayed-on coating, the concentration may range by weight from about 2.5% to 17.5% of SiO_2 equivalent.

EXAMPLE 2

The method of aluminizing described in Example 1 is repeated in the coating of a vane shroud made of 17–4 pH stainless steel (17% Cr, 4% Ni, 3% Cu and the balance essentially iron). Because of the configuration of the shroud, special care is taken in preparing the shroud for pack aluminizing using substantially the same pack and conditions described in Example 1. Following the pack aluminizing step, the shroud is cleaned of adhering pack material and then coated with the silicate salt which is thereafter cured, and the conversion coating applied and cured in the manner similarly herein.

It is believed that the baking of the duplex silicate-conversion coating results in a reaction product which provides new and improved resistance to corrosion in saline environments. While the silicate is preferably first applied to the thermally aluminized surface, it is appreciated that it can be applied as a solution together with the conversion coating materials. Thus, the conversion coating solution prior to spraying may contain about 0.05 to 2% by weight SiO_2 equivalent as sodium silicate, potassium silicate, ethyl silicate, and the like.

As will be appreciated, the amount of silicate dissolved in the conversion coating solution will depend upon the prevailing pH of the solution, and therefore, the amount of silicate dissolved therein will be limited to some extent. However, the silicate dissolved in the solution will generally be sufficient to enhance the corrosion resistance of the ferrous article, since the silicate during the coating process tends to migrate to the aluminized surface and provide the necessary barrier function and to react with the conversion coating during the curing cycle. In this connection, reference is made to Test No. 3 in which the conversion coat applied to the specimen also contains sodium silicate.

It will be appreciated that in addition to the conversion coating formulation described herein; various conversion coatings of the phosphate-chromate types may be employed in conjunction with the soluble silicate salt. Stating it broadly, the conversion coating comprises phosphates and chromates of at least one metal, for example, Al, Mg, Zn, Be, Ba, Sr, Ce, group metals and other metals. As a preferred embodiment, a conversion coat containing phosphates and chromates of aluminum and magnesium has been found very desirable.

As illustrative of other conversion formulations, the following examples are given:

A phosphate-chromate solution X of beryllium is produced by starting with 200 ml. of 85% phosphoric acid (1.6 grams/mil) which is diluted with water to a pH of 1.01. To the solution is added 62.5 grams of chromic acid (99% CrO_3) and 40 grs. of beryllium phosphate

$$(Be_3(PO_4)_2)$$

This solution has a density of about 1.2 grams/mil and provides a conversion coating by spraying the solution onto the aluminized surface and curing at temperatures ranging from 300° F. (150° C.) to 800° F. or 900° F. (425° C.–482° C.), the spraying and curing being repeated about three times or more, if necessary.

The foregoing solution may be used as a base to which other soluble metal salts or compounds can be added. A preferred formulation is to add 0.69 gram of the other metal salt or compound to 120 grams of solution X. The

following series of conversion solutions are illustrative of the various types of solutions that can be made:

(1) 0.69 gram of magnesium chromate dissolved in 120 grams of solution X at a pH of 1.8.
(2) 0.69 gram of magnesium phosphate dissolved in 120 grams of solution X at a pH of 1.3.
(3) 0.69 gram of aluminum phosphate dissolved in 120 grams of solution X at a pH of 2.
(4) 0.69 gram of $Ba(OH)_2 \cdot 3H_2O$ dissolved in 120 grams of solution X at a pH of 1.8.
(5) 0.69 gram of $Ce_2(CO_3)_3 \cdot 5H_2O$ dissolved in 120 grams of solution X at a pH of 1.9.
(6) 0.69 gram of $Ce(PO_3)_3$ dissolved in 120 grams of solution X at a pH of 1.4.

Sprayed coatings produced from the foregoing solutions and then dried and cured on a steel substrate exhibited satisfactory conversion coating properties when subjected to a series of oxidation and salt spray cycles.

Broadly speaking, the conversion solutions may range in composition by weight of at least about 0.5% of at least one phosphate and chromate-forming metal, e.g. about 0.5 to 10%, about 5% to 30% phosphoric acid, about 3% to 8% chromic acid (CrO_3) and the balance essentially water. A preferred conversion solution is one containing by weight about 0.02% to 3% dissolved aluminum, about 0.75% to 6% dissolved magnesium, about 5% to 30% phosphoric acid (preferably 15% to 30%), about 3% to 8% chromic acid and the balance essentially water. A more specific composition is one containing by weight about ¼% aluminum, about 1.5% magnesium, about 15% phosphoric acid, about 5% chromic acid and the balance essenentially water.

As stated hereinbefore, the silicate salt may be selected from the group consisting of sodium silicate, potasium silicate, lithium silicate, and organic silicates, such as ethyl silicate.

The ASTM salt spray test (Designation B117–64) employed in testing the resistance to corrosion of the various coating systems disclosed herein comprises a fog chamber, a salt solution reservoir, a supply of suitably conditioned compressed, one or more fog nozzles, specimen supports, provisions for heating the chamber and control means. The specimens are supported or suspended between 15 and 30 degrees from the vertical (out of contact with each other) and preferably parallel to the principal direction of horizontal flow of fog through the chamber. The salt solution is made up of 5±1 parts of salt to 95 parts of distilled water containing not more than 200 p.p.m. of total solids. The condensed fog should have a pH of about 6.5 to 7.2. The temperature within the chamber is maintained at 95° F. plus 2° or minus 3° F. For the specimens in this case, the salt spray testing is carried out for a period of 5 hours, precautions being taken to avoid dripping of condensed solution from one specimen to another.

Although the present invnetion has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

What is claimed is:

1. A method of improving the corrosion resistance of a ferrous metal article which comprises,
providing such article with a thermally aluminized surface characterized by the presence of iron aluminide,
applying to the aluminized surface of said article a coating from a solution of a soluble silicate salt selected from the group consisting of sodium silicate, potassium silicate, lithium silicate and ethyl silicate, at a temperature ranging up to about 100° C.
removing excess liquid from said surface so as to form a uniform layer of said silicate salt covering said surface,
and then drying said layer.

2. The method of claim 1, wherein the dried layer is cured by heating said surface to a temperature of about 150° to 430° C.

3. The method of claim 1, wherein the step of applying the silicate layer is repeated a plurality of times, and wherein the layers are thereafter cured by heating at a temperature of about 150° C. to 430° C.

4. A method of improving the corrosion resistance of a ferrous metal article which comprises subjecting said article to the steps of
providing said article with a thermally aluminized surface characterized by the presence of iron aluminide,
applying a coating from a solution of a silicate salt selected from the group consisting of sodium silicate, potassium silicate, lithium silicate and ethyl silicate to said aluminized surface at a temperature ranging up to about 100° C.
removing excess liquid from said surface to assure a layer of said silicate salt on said surface following which the layer is dried,
repeating the foregoing cycle of steps at least once to produce a uniform silicate coating of adequate thickness,
and then curing said silicate coating by heating at a temperature of about 150° C. to 430° C.

5. A method of improving the corrosion resistance of a ferrous metal article which comprises,
providing said article with a thermally aluminized surface characterized by the presence of iron aluminide,
providing said ferrous article with a thermally aluminized surface, characterized by the presence of iron aluminide, applying an adherent surface layer of a silicate salt selected from the group consisting of sodium silicate, potassium silicate, lithium silicate and ethyl silicate,
applying a conversion coating on said surface from a solution containing by weight about 5% to 30% phosphoric acid, about 3% to 8% chromic acid (CrO_3), and at least about 0.5% of at least one chromate and phosphate-forming metal and the balance essentially water,
drying said conversion coating,
and then thermally curing said conversion coating.

6. The method of claim 5, wherein aluminum and magnesium are chromate and phosphate-forming metals in amounts ranging from about 0.02% to 3% aluminum and about 0.75% to 6% magnesium.

7. The method of claim 6, wherein the conversion solution comprises by weight about ¼% aluminum, about 1.5% magnesium, about 15% phosphoric acid, about 5% chromic acid and the balance essentially water.

8. A method of improving the corrosion resistance of a ferrous metal substrate which comprises,
providing said substrate with a thermally aluminized surface characterized by the presence of iron aluminide,
applying to the aluminized surface of said article a coating from a solution containing a salt selected from the group consisting of sodium silicate, potassium silicate, lithium silicate and ethyl silicate together with chromates and phosphates of at least one metal,
and then curing said coating.

9. The method of claim 8, wherein the solution contains chromates and phosphates of aluminum and magnesium and wherein the coating is cured at a temperature of about 150° C. to 430° C.

10. The method of claim 9, wherein the solution contains by weight about 0.05 to 2% SiO_2 equivalent, about 5% to 30% phosphoric acid, about 0.02% to 3% aluminum, about 3% to 8% chromic acid, about 0.75% to 6% magnesium and the balance essentially water.

11. A method of improving the corrosion resistance of a ferrous metal substrate which comprises,

providing said ferrous metal with a thermally aluminized surface characterized by the presence of iron aluminide,

applying a coating to said substrate from a solution containing a dissolved silicate corresponding in amount to about 0.1% to 2% by weight of SiO_2 equivalent followed by curing and repeating said step at least once,

applying a second coat from a silicate, solution containing by weight about 2.5% to 17.5% of SiO_2 equivalent, followed by curing and repeating said step at least once,

applying a conversion coat to said second coat followed by curing and repeating said step at least once,

and then applying a silicate coat to said conversion coat from a solution containing about 2.5% to 17.5% by weight of SiO_2 equivalent followed by curing and repeating said step at least once.

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