STRUCTURAL STEEL MEMBERS AND METHOD OF MAKING SAME

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ABSTRACT OF THE DISCLOSURE

A method of making a steel facing in which a steel body having up to 0.12% carbon, 0.25 to 0.75% silicon, 0.20 to 0.50% manganese, 0.07 to 0.15% phosphorus, up to 0.05% sulphur, 0.25 to 0.55% copper, 0.3 to 1.25% chromiunm, up to 0.65% nickel, balance iron, is prerusted with an aqueous solution of copper sulphate or nickel sulphate and iron nitrate. After drying of the prerusted solution and after-moisturizing, a film-forming layer of elastomer, synthetic resin, cellulose, wax or a film-forming silicate is applied. The film-forming layer is penetrable by vapor but not by liquid and gradually weathers away to expose the rust layer.

The present invention relates to a method of treating light-alloy steel bodies for improving the surface characteristics thereof, e.g., preventing corrosion, in order to render the steel members suitable for use in exposure to the atmosphere as panels, profiles or the like in above-surface structures; more particularly, this invention relates to improvements in the surface treatment of steel bodies to modify surface-corrosion characteristics and improve corrosion resistance.

In buildings, bridges and other above-surface structures, the application of steels has generally been such as to disadvantage that they are easily concealed or encased because of the tendency to corrosion, the unsatisfactory characteristics of atmospheric corrosion, the mottled appearance of the steel members after prolonged weathering, and the inability to protect such steel surfaces permanently by painting or the like. Thus, although steel structural members are commonly employed in buildings because of their great strength, it has been the practice to encase the structural members in concrete or to mount panels upon them. In modifications of this approach, a steel member may be jacketed with a corrosion-resistant and aesthetic layer of another metal (e.g., stainless steel, aluminum or an aluminum alloy) such that the cladded steel member can be exposed to the atmosphere without these disadvantages. In panel-type constructions, moreover, it has not been possible to make use of the relatively inexpensive steels easily fabricated into panels and surface members because of the poor corrosion characteristics of the bodies. In panel construction, therefore, the use of anodized (electrolytically oxidized) aluminum or aluminum alloy sheets is prevalent, although stainless steel laminates or sheets have been employed. 18-8 chromium-nickel stainless steels have, however, the significant disadvantage that they are extremely expensive and similar disadvantages inherent when chromium-nickel-molybdenum steel alloys serve to cover or encase the steel structural members. In order to keep the expense down, laminates of aluminum, aluminum alloy, stainless steel or the like are formed by bonding such surfacing materials to one or both sides of a steel plate or structural member (a profile beam or column) with increased fabrication cost.

It has, therefore, long been sought in the construction and metallurgical fields to provide a steel structural member whose surfaces are able to weather prolonged exposure to corrosive environments and the atmosphere and which is reasonable pleasant in appearance. It has been found that certain types of steels are capable of rusting or oxidizing relatively uniformly under such conditions that the oxide layer resists further corrosion. Such members have not, however, found widespread use since the oxide layer, at least initially, has a tendency to stain adjoining nonmetallic surfaces as moisture carries part of the oxide onto these adjoining surfaces. In general these members are erected or used without the application of a protective coating so that, upon exposure to the atmosphere, the self-protecting oxide layer, resistant to further corrosion, is formed as an oxide patina. Steels of this type generally include corrosion-resistant components such as copper, nickel, chromium, vanadium and phosphorous individually or in combination and made up at most 2% by weight of the alloy. It has been found that such steels do not ensure a satisfactory bond of the oxide layer to the steel substrate and indeed, the oxide layer of these members is not unlike the loose oxides formed on common steel and iron bodies. Only after a prolonged exposure to the atmosphere is the oxide film built up to a sufficient thickness to prevent further deterioration of the steel body. The staining of the joining surfaces is also a characteristic of these members which have a mottled appearance with weathering.

It is, accordingly, the principal object of the present invention to provide an improved steel structural member, adapted to be used in direct exposure to the atmosphere in building construction or the like whose surface characteristics are aesthetically pleasing, unaffected by prolonged exposure to the atmosphere and to other corrosive environments, and remain uniform without staining adjoining nonmetallic surfaces.

A further object of this invention is to provide an unclad steel member suitable for use as the surfacing member of structural steel elements and in building structures or the like, which is of relatively low-cost and easily produced.

Still another object of this invention is to provide a method of treating steel bodies (e.g. steel sheets, plates, bars and structural steel profiles) in order to render their surfaces aesthetically pleasing, to impart a uniform coloration to the surfaces, to improve the resistance to corrosion of the surfaces of the member, and to enable the members to withstand prolonged weathering without substantial modification of its surface characteristics and appearance.

I have found, in accordance with the present invention, that these objects can be attained by treating steel bodies of light-alloy steels with a presurfacing solution to form an initial oxide layer strongly bonded to the underlying metal and free from tendencies to loosen under atmospheric exposure, but able to oxidize further to produce a dense oxide layer. Bodies of this nature can be used as panels or the like in buildings, structures and to encase or conceal the structural members of substantially any above-surface structure by completely encasing such steel members or overlying only those portions exposed to the atmosphere. According to a feature of this invention, the initial oxide structure is stabilized by depositing thereon a water impermeable but vapor-penetrable layer of a film-forming composition.

In accordance with one aspect of this invention, the prestructuring solution, adapted to generate the initial oxide film, comprises a water soluble iron salt convertible into iron oxide upon treatment of the metal surface thereof and at least one heavy metal sulfate adapted to
form basic sulfates—upon exposure to the atmosphere—which are scarcely soluble in water; the film-forming layer consists of a film-forming substance selected from the group which consists of resins and/or synthetic resins, waxes, cellulose film formers, rubber and other elastomeric derivatives, silicates or the like, used together or individually. While various steel alloys can serve as the treated substrate of the present invention, it has been found that best results are obtained when the light-alloy steel contains less than 2% by weight of copper, nickel, chromium, vanadium, molybdenum and phosphorus individually or in combination with at least copper and chromium being part of the alloy in a ratio of at least 1 to 1. A suitable composition for the purposes of the present invention contains:

- Trace amounts to 0.12% carbon; 0.25 to 0.75% silicon; 0.20 to 0.50% manganese; 0.07 to 0.15% phosphorus; trace amounts to 0.05% sulphur; 0.25 to 0.55% copper; 0.30 to 1.25% chromium; trace amounts to 0.65% nickel; the balance being iron (all percents by weight).

The prereusting solution should also include a viscosity modifier (e.g. glycero) adapted to ensure a smooth and uniform coating of the prereust liquid upon the steel body; a wetting agent (preferably a fatty acid condensate with methyl taurine) to promote intimate contact between the coating solution and the substrate; and a volatile water-miscible component (e.g. alcohol) adapted to vaporate after coating of the metal surface to facilitate drying of the prereust-treatment liquid. Furthermore this solution should contain a component (e.g. oxalic acid) designed to promote the formation of fine-grain iron oxide upon the metal surface with drying of the treatment liquid.

According to a more specific feature of this invention, the iron salt is present in the treating solution in an amount ranging between 5 and 35 weight percent, while the heavy metal salt is present in an amount ranging from 0.1 to 4 weight percent. The heavy metal sulfate component should include salts of at least copper and nickel so that best results are obtained when copper sulfate is present in an amount ranging between 0.1 and 2% by weight and nickel sulfate is present in an amount ranging from 0.1 to 2% by weight as well. The treatment solution thus may also contain 0.1 to 1% weight glycerine, 0.1 to 2% by weight of the component (e.g. oxalic acid) promoting fine-grain oxide formation, from 0.01 to 0.1% by weight of the wetting agent, from 10 to 50% by weight of the volatile water miscible component and the balance water.

Following drying of the treatment solution upon this light-alloy steel surface mentioned above, it has been found highly advantageous and thus is an important feature of this invention that the treated surface is subjected to an after-moisturization or wetting with an aqueous solution advantageously containing a water-miscible volatile component (e.g. alcohol). It has been found that an after-moisturization of the treated surface with, for example, a wetting solution consisting of 80 to 90% by weight water and 5 to 20% by weight alcohol, results in the formation of a relatively uniform initial rust structure or surface matrix which withstands abrasive action. In the absence of the after-moisturization treatment, the initial rust structure is formed significantly more slowly.

As indicated earlier, it is an important feature of this invention that, subsequent to the formation of the initial rust structure, a layer of at least one film-forming substance is provided upon the oxide treated steel surface. The film-forming solution, in accordance with this invention may include any of the known film formers mentioned earlier but most advantageously consists of an elastomeric material (e.g. a synthetic hydrocarbon such as carbon tetrachloride), a shedding component (e.g. a colloidal silica such as that marketed under the name Aerosil), a pigment component, and a high molecular weight alcohol component. Upon application of such a film-forming solution is found to be liquid repellent but permeable to water vapor and gases so that penetration of vapors through the film-forming layer enhances the development of the progressive and aesthetic oxide layer therein, while the water-repellency prevents the oxide layer from coming into contact with adjoining substrates and becoming discolored by weathering. In the film-forming layer, the elastomeric material advantageously constitutes 5 to 40% by weight, the easily vaporizable solvent between 40 and 90% by weight, and the colloidal silica or other "shedding" component between 2 and 20% by weight, with the other components each making up between 0.1 and 2% by weight.

Thus, according to the principle of the present invention, a method of making steel members for panels, structural surfaces and the like comprises the steps of treating the light-alloy steel body with an iron-containing prereust solution and permitting this solution to dry upon the surface of the steel body; after moisturizing the treated surface of the body to promote the formation of the fine-grain initial oxide structure or matrix; thereafter coating the surface with a film-forming substance repellent to water vapor; and exposing the film-coated surface of the metal body to atmospheric conditions whereby atmospheric oxidation continues below the film-forming layer. Bodies produced in this manner can be used as facing sheets for panel constructions, for encasing structural members and as decoration or protecting members upon any structural elements since the oxide layer becomes progressively thicker under the influences of corrosive atmospheres. It appears that both the iron salt (preferably iron nitrate) and the heavy metal sulfates (preferably copper and/or nickel sulfate) are required in the prereust solution to ensure an adherent uniform and fine-grain initial rust formation which is subjected to further oxide formation through the film-forming layer.

The film-forming layer is self-shedding and, for this purpose, may be provided with one or more chalk-like substances or chalk-forming substances designed to permit the film-forming layer to wear away with time and directly expose the underlying oxide layer which, because of the further oxidation described above, attains a final thickness prior to wearing away of the protective film sufficient to prevent further corrosion of the steel body.

The film-forming layer preferentially contains between 10 and 20% of the elastomeric material, synthetic resin or colloide film former, between 50 and 70% of a solvent for the latter, between 5 and 10% of a chalk-forming or shedding-promoting component (e.g. silica, silica gel, alumina stearate, zinc stearate) or a carbonate salt (e.g. calcium carbonate) (all percentages by weight).

A further component of the film-forming layer may be the high-carbon number alcohol which serves to de-moisturize or dry the underlying oxide layer.

According to a more specific feature of this invention, the film-forming layer also includes at least one pigmen-titious material designed to impart to the protective film, a coloration corresponding to the deepest oxide patina which will develop upon further oxidation through the film-forming layer. Thus, upon the wearing away of the film-forming layer, no disoloration arises since the film worn away corresponds in color to the developed coloration of the underlying oxide layer.

The above described process and advantages of the present invention will become readily apparent from the following description, reference being made to the accompanying drawing in which the sole figure is a diagrammatic cross section through a steel panel treated in accordance with the present invention.

In the drawing, I show a steel panel 1 which has been treated with the prereust solution on both of its surfaces.
The initial rust layers are subjected to after-moisturization to form the initial oxide layers upon the opposite surfaces of the sheet. The initial rust layers are coated with self-shedding protective films which are repellent or impermeable to liquid water but are gas or vapor permeable. After the forming of such coatings, the panel or profile can be used upon structures in the conventional manner as facing material in direct exposure to the atmosphere. Inasmuch as the protective layer is gas-permeable and the initial rust layer is a relatively porous layer, oxide formation occurs below the initial rust layers 2 to a depth represented by the dot-dash lines 4. The final oxide layer is then represented by the thicknesses 5 and develops to a depth sufficient to bar further corrosion of the steel body. Continued exposure of the panels to the atmosphere results in a weathering away or stripping of the layers 3 to expose the oxide layers 5 directly. The oxide layers 5 are found to be strongly adherent to the substrate, to be of uniform coloration and, when the self-shedding layers are pigmented to correspond to the coloration of the final oxide layers 5, no change in color will be observed with the shedding of the layers 3.

### EXAMPLE

Two steel panels (sheets) and a steel profile were used with the following compositions (all percents by weight):

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.05</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.25</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.20</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.07</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.01</td>
</tr>
<tr>
<td>Copper</td>
<td>0.25</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.39</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.66</td>
</tr>
<tr>
<td>Iron</td>
<td>0.16</td>
</tr>
</tbody>
</table>

The following prerust solutions were employed (all percents by weight):

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron nitrate</td>
<td>15 20 25</td>
</tr>
<tr>
<td>Copper sulfate</td>
<td>0.4 0.6 0.8</td>
</tr>
<tr>
<td>Nickel sulfate</td>
<td>0.4 0.6 0.8</td>
</tr>
<tr>
<td>Glycol</td>
<td>0.1 0.1 0.1</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>0.1 0.1 0.1</td>
</tr>
<tr>
<td>Alcohol (trademark for fatty acid condensate with sodium methyl taurinate)</td>
<td>0.02 0.02 0.02</td>
</tr>
<tr>
<td>Water</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The following film-forming solutions were used (all percentages by weight):

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclocaoutchous</td>
<td>10 16 20</td>
</tr>
<tr>
<td>Avrool (silica colloidal)</td>
<td>10 10 10</td>
</tr>
<tr>
<td>Iron oxide (hydrate)</td>
<td>2 2 2</td>
</tr>
<tr>
<td>Cy high-carbon-number alcohol</td>
<td>2 2 2</td>
</tr>
<tr>
<td>Carbon tetrachloride (balance)</td>
<td>76 70 59</td>
</tr>
</tbody>
</table>

The following after-moisturization solutions were used (all percentages by weight):

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>80 90 95</td>
</tr>
<tr>
<td>Ethyl alcohol (industrial grade)</td>
<td>20 30 5</td>
</tr>
</tbody>
</table>

A steel body of each of the aforesaid compositions was coated uniformly with each of the prerust solutions given above by spraying or brushing and the prerust solution permitted to dry. Thereafter, each of the specimens treated with the prerust solution, which dried rapidly (in a matter of minutes), was subjected to the after-moisturization treatment with each of the solutions as given and it was found that within about a half hour, each of the specimens had developed a relatively thin uniform and adherent initial rust structure with a brownish coloration. No significant chemical attack upon the steel surface was observed.

Upon the initial rust structure of each of the specimens, each of the film-forming solutions set forth above was used along a portion of the specimen and applied by spraying and brushing. In both cases, uniform coatings were obtained. Upon drying, the resulting film was found to stabilize the initial rust structure against mechanical abrasion. When the film-coated steel surfaces were subjected to high-velocity streams of water, no migration of the initial rust structure was observed and indeed the surfaces appeared to be completely impermeable to water.

Thereafter, the specimens were subjected to accelerated corrosion tests at an elevated temperature in air at high relative humidity and a gradual deepening of the brownish coloration was noted. Examination showed the development beyond the initial rust structure of a deep oxide patina which was relatively thick and adherent to the steel substrate. Further treatment of the bodies with high-velocity jets of water failed to displace the oxide layer and, when the bodies were used as exterior facings of buildings, as sheathing for steel structural members, as panels and a structural member in direct exposure to the atmosphere, no coloration of adjoining surfaces was observed in spite of the fact that the bodies were exposed to ambient atmospheric conditions for prolonged periods. When similarly prepared members were used in structures without accelerated oxidation immediately after drying and setting of the film, a slower development of the oxide layer below the film was discerned and the deepening of the oxide layer was found to be completely uniform in spite of the greater exposure of some parts of the members, by comparison with others, to the elements.

After prolonged stand in the atmosphere, it was found that weathering effects caused decomposition or removal of the film layer, whereupon the hitherto coated oxide layer was directly exposed. The thick oxide layer formed prior to this loss of the film layer remained tenaciously adherent to the steel body and prevented further oxidation thereof.

It was found that similar results could be obtained when equivalent quantities of a synthetic resin and solvent (e.g. polyethylene and chlorinated hydrocarbon solvents) were substituted for the elastomeric component and its solvent. Similar results were also obtained with cellulose acetate/alcohol combinations and paraffin wax/carbon tetrachloride substitutions. While colloidal silica was found to be most advantageous for the silica component, other dulling compositions can be substituted in equivalent quantities. Suitable compositions for this purpose were found to be silica gel, aluminum stearate, zinc stearate, and carbonate salts of alkali and alkaline-earth element. The addition of pigments to the film-forming layer served to mask the developing coloration of the underlying oxide layer and imparted a uniform coloration to the surface which remained after the weathering and stripping of the film layer because of the deeper shade of the coloration of the oxide layer. Thus sufficient pigment (e.g. iron oxide hydrate) was added to the film-forming layer to impart thereto a coloration essentially identical with that which develops with increased thickening of the oxide layer. Additional components of the film-forming solution can include plasticizers for the elastomer or resin designed to increase its flexibility, dryers to eliminate any tackiness, and high-molecular-weight al-
cohols adapted to absorb moisture from the underlying layer.

I claim:

5 1. A method of making a steel facing for structures and the like comprising the steps of:
   treating at least one surface of a steel body having substantially the following composition:
   trace amounts to 0.12% by weight carbon,
   0.25 to 0.75% by weight silicon,
   0.20 to 0.50% by weight manganese,
   0.07 to 0.15% by weight phosphorus,
   trace amounts to 0.05% by weight sulphur,
   0.25 to 0.55% by weight copper,
   0.30 to 1.25% by weight chromium,
   trace amounts to 0.65% by weight nickel,
   the balance being iron,

   with a prerust solution in the form of an aqueous solution of a water-soluble iron salt and at least one heavy-metal sulfate to form an initial rust-structure layer thereon;

   subjecting the surface to further oxidation in an oxidizing atmosphere; and

   stabilizing said initial rust-structure layer by coating same with a liquid-impermeable but vapor-permeable film prior to said further oxidation.

2. The method defined in claim 1 wherein said film is composed at least in major part of an elastomer, a synthetic resin, a cellulosic material, a wax or a film-forming silicate, and contains a shedding component facilitating weathering away of said film to expose the rust layer.

3. The method defined in claim 2 wherein said component is selected from the group which consists of siliceous materials, aluminum stearate, zinc stearate, and carbonate salts.

4. The method defined in claim 3 wherein said film contains a pigment for imparting thereeto a coloration approximately corresponding to the coloration of the rust layer upon the further oxidation of said body through said film.

5. The method defined in claim 1 wherein said heavy metal sulfate is selected from the group which consists of copper sulfate and nickel sulfate and said iron salt is iron nitrate.

6. The method defined in claim 1, further comprising the steps of drying said prerust solution upon said surface, and thereafter treating the surface with an aqueous after-moisturizing solution.

7. A method of making a steel facing for structures and the like comprising the steps of:
   treating at least one surface of a steel body with a prerust solution to form an initial rust-structure layer thereon;

   subjecting the surface to further oxidation in an oxidizing atmosphere; and

   stabilizing said initial rust-structure layer by coating same with a liquid-impermeable but vapor-permeable film prior to said further oxidation, said body having the following composition (all percents by weight):
   trace amounts to 0.12% carbon,
   0.25% to 0.75% silicon,
   0.20% to 0.50% manganese,
   0.07% to 0.15% phosphorus,
   0.25% to 0.55% sulphur,
   0.30% to 1.25% chromium,
   trace amounts to 0.65% nickel, and
   the balance being iron,

   said prerust solution being an aqueous solution containing (all percents by weight):
   between 5% and 35% of a water-soluble iron salt,
   between 0.1% and 4% of at least one heavy metal salt selected from the group consisting of copper sulfate and nickel sulfate,
   between substantially 0.1% and 1% glycercine,
   between substantially 0.1% and 2% oxalic acid, and
   between substantially 10% and 50% alcohol;

   drying said prerust solution upon said surface; and

   after-moisturizing the surface so treated with a solution consisting essentially of 80% to 95% by weight water and 5% to 20% by weight alcohol, said film being formed on said rust-structure layer by applying thereto a film-forming solution consisting essentially of (all percents by weight):
   5% to 40% of a film-forming substance,
   40% to 90% of a solvent for said film-forming substance,
   2% to 20% of a shedding component facilitating weathering of the film upon oxidation of said body therethrough,

   0.1% to 2% of a pigment imparting to said film a coloration corresponding essentially to the coloration of said rust-structure layer upon further oxidation of said body through said film, and

   0.1% to 2% of a component adapted to demoisturize said rust-structure layer.

8. The method defined in claim 7, further comprising the step of applying said steel body to an above-surface structure as a facing element whereby the further oxidation of the rust-structure layer and the weathering away of said film is effected in ambient atmosphere.


10. A vapor-permeable/liquid-impermeable-film solution for application to a rusted steel structure and adapted to weather away gradually to reveal the rust surface, comprising 5% to 40% by weight of a film-forming substance selected from the group which consists of an elastomer, a synthetic resin, a cellulosic material, a wax and a film-forming silicate; 40% to 90% by weight of a solvent for said film-forming substance; 2% to 20% by weight of a shedding component facilitating weathering away of the film upon oxidation of an iron body therethrough; 0.1% to 2% by weight of a pigment imparting to said film a coloration corresponding essentially to the coloration of a rust structure beneath that film upon oxidation of an iron body therethrough; and 0.1% to 2% by weight of a component adapted to demoisturize said rust structure.

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