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Title: METHODS OF REMOVING RUST FROM A FERROUS METAL-CONTAINING SURFACE

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METHODS OF REMOVING RUST FROM A FERROUS METAL-CONTAINING SURFACE

FIELD OF THE INVENTION

[0001] The present invention relates to, among other things, methods for removing rust from a ferrous metal-containing surface.

BACKGROUND OF THE INVENTION

[0002] During processing or simply upon exposure to the atmosphere, a metal oxide layer, i.e., rust, is often formed over all or part of a ferrous metal surface, thereby impairing its appearance and/or suitability for further use. One example is steel, such as mild steel used in the manufacture of various articles. Accordingly, it is often desirable to remove the metal oxide layer. Conventionally, this removal has been accomplished by treating the rusted metal surface with a strong acid, such as nitric, sulfuric, hydrochloric, or phosphoric acid. These highly acidic, corrosive and caustic chemicals are, however, often undesirable from an environmental and safety standpoint.

[0003] In some cases, the ferrous metal to be treated is oriented in a substantially vertical fashion such as can be the case with, for example, large structures, such as storage tanks, ships and other vehicles, and bridges, among many others. In addition, sprayable products are often desired for convenience and efficiency of use.

[0004] It would, therefore, be desirable to provide methods of removing rust from a ferrous metal-containing surface, including those that are oriented in a substantially vertical fashion, by using a sprayable composition that does not include strong acids that are environmentally undesirable.

SUMMARY OF THE INVENTION

[0005] In certain respects, the present invention is directed to methods for removing rust from a ferrous metal-containing surface. The methods comprise contacting the surface with a composition comprising: (a) a carboxylic acid; (b) a synthetic hectorite clay; and (c) water. The present invention also relates to, inter alia, ferrous metal-containing surfaces treated by the foregoing methods.
DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0006] For purposes of the following detailed description, it is to be understood that the invention may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in any operating examples, or where otherwise indicated, all numbers expressing, for example, quantities of ingredients used in the specification and claims are to be understood as being modified in all instances by the term “about”. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0007] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

[0008] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of “1 to 10” is intended to include all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10. In this application, the use of the singular includes the plural and plural encompasses singular, unless specifically stated otherwise. In addition, in this application, the use of “or” means “and/or” unless specifically stated otherwise, even though “and/or” may be explicitly used in certain instances.

[0009] As indicated, certain embodiments of the present invention are directed to methods for removing rust from a ferrous metal-containing surface. As used herein, “rust” refers to a coating or film formed on a metal by oxidation or corrosion. In some cases, the rust that is removed in the methods of the present invention is “red rust” which, as used herein, refers to a coating or film formed on iron or steel by oxidation, as during exposure to air and/or moisture, that comprises iron (II) oxide (FeO, wüstite), alpha phase iron (III) oxide (α-Fe₂O₃, hematite), beta phase iron (III)
oxide ($\beta$-$\text{Fe}_2\text{O}_3$), gamma phase iron (III) oxide ($\gamma$-$\text{Fe}_2\text{O}_3$, maghemite), epsilon phase iron (III) oxide ($\epsilon$-$\text{Fe}_2\text{O}_3$), iron (II) hydroxide ($\text{Fe(OH)}_2$), iron (III) hydroxide ($\text{Fe(OH)}_3$, bernalite), and/or hydrated forms and combinations of any of the foregoing. In some embodiments, the iron oxide that is removed in the methods of the present invention is of a type that is often referred to as “mill scale” which, as used herein, refers to a coating or film formed on iron or steel by oxidation, as during exposure to air, moisture, and/or heat, that comprises iron(II,III) oxide ($\text{Fe}_3\text{O}_4$, magnetite), alpha phase iron (III) oxide ($\alpha$-$\text{Fe}_2\text{O}_3$, hematite), iron(II) hydroxide ($\text{Fe(OH)}_2$), (III) hydroxide ($\text{Fe(OH)}_3$, bernalite), and/or hydrated forms and combinations of any of the foregoing.

[0010] Metal surfaces that may be treated in the methods of the present invention include, but are not limited to, surfaces constructed of cold rolled steel, hot rolled steel, steel coated with zinc metal, zinc compounds, or zinc alloys, such as electrogalvanized steel, hot-dipped galvanized steel, galvanealed steel, and steel plated with zinc alloy. Surfaces constructed of mild steel may be treated in the methods of the present invention. Mild steel, as used herein, refers to low carbon steel containing less than 0.25% by weight carbon.

[0011] In the methods of the present invention, the metal surface is contacted with a composition comprising a carboxylic acid. In certain embodiments, the carboxylic acid selected for use in the compositions described herein has a water solubility of $> 1$ g/L at 20°C. Carboxylic acids suitable for use in the compositions used in the methods of the present invention include, for example, monocarboxylic acids, such as formic acid, acetic acid, propionic acid, methylacetic acid, butyric acid, ethylacetic acid, n-valeric acid, n-butanecarboxylic acid, acrylic acid, propiolic acid, methacrylic acid, palmic acid, stearic acid, oleic acid, linolic acid, and linolenic acid; dicarboxylic acids, such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, lepargilic acid, sebacic acid, maleic acid, and fumaric acid; aliphatic hydroxy acids, such as glycolic acid, lactic acid, tartaronic acid, glyceric acid, malic acid, tartaric acid, citramalic acid, citric acid, isocitric acid, leucine acid, mevalonic acid, pantoic acid, recinoleic acid, ricinelaic acid, cerebronic acid, quinic acid, and shikimic acid; aromatic hydroxy acids, such as salicylic acid, creosote acid, vanillic acid, syringic acid, pyrocatechuic acid, resorcylic acid, protocatechuic acid, gentisic acid, orsellinic acid, gallic acid, mandelic acid, benzilic acid, atrolactic acid, melilotic acid, phloretic acid, coumaric acid, umbellic
acid, caffeic acid, ferulic acid, and sinapic acid. Mixtures of any of the foregoing may also be used.

[0012] In certain embodiments, the carboxylic acid is present in the composition used in the methods of the present invention in an amount of at least 1 percent by weight, such as at least 10 percent by weight, or, in some cases, at least 15 percent by weight, with the weight percents being based on the total weight of the composition. In certain embodiments, the carboxylic acid is present in the composition used in the methods of the present invention in an amount of no more than 50 percent by weight, such as no more than 30 percent by weight, or, in some cases, no more than 25 percent by weight, with the weight percents being based on the total weight of the composition.

[0013] In the methods of the present invention, the composition that is contacted with the ferrous metal-containing surface also comprises a synthetic hectorite clay. The presence of a synthetic hectorite clay in the presently described compositions produces a thickened composition with a highly shear thinning, thixotropic rheology. As a result, the composition is sprayable using typical spray devices (including those mentioned below) and yet, it has been discovered, remains on the ferrous metal-containing surface, even if the surface is oriented substantially vertically, for a sufficient time to effect rust removal. As used herein, the term “substantially vertically” means substantially perpendicular (i.e., within ± 20% from perpendicular) to the ground or other surface upon which the ferrous metal-containing surface is disposed. Indeed, it was a surprising discovery that the use of a synthetic hectorite clay, as opposed to other thickening agents, including other thixotropic clays (such as kaolin and bentonite clays), produces a composition that is both sprayable at ambient conditions and can be effective in removing rust from a ferrous metal-containing surface even when the surface is oriented substantially vertically. It is currently believed that the amount of other thixotropic clays that would be needed to produce an effective composition for rust removal from a substantially vertically oriented surface would result in a composition that is not sprayable at ambient conditions. As used herein, “ambient conditions” refers to 23°C and atmospheric pressure.

[0014] Synthetic hectorite clays that are suitable for use in the compositions described herein include, for example, LAPONITE RD, LAPONITE RDS, and
LAPONITE JS, including combinations thereof. As will be appreciated, each of these is a layer-structured hydrous magnesium silicate according to the chemical formula NaO3(Mg, Li)2Si3O10(F, OH)2. LAPONITE RD is a free flowing synthetic layered silicate having a bulk density of 1,000 kg/m³, a surface area (BET) of 370 m²/g, a pH of a 2% suspension in water of 9.8, wherein the composition on a dry basis by weight is 59.5% SiO₂, 27.5% MgO, 0.8% Li₂O, and 2.8% Na₂O. LAPONITE RDS is also a free flowing a free flowing synthetic layered silicate having a bulk density of 1,000 kg/m³, a surface area (BET) of 330 m²/g, a pH of a 2% suspension in water of 9.7, wherein the composition on a dry basis by weight is 54.5% SiO₂, 26.0% MgO, 0.8% Li₂O, 5.6% Na₂O, and 4.1% P₂O₅. The particle size of the synthetic hectorites, such as those described above, is typically 1 to 30 nanometers in average diameter.

[0015] In certain embodiments, the synthetic hectorite clay is present in the composition used in the methods of the present invention in an amount of at least 1 percent by weight, such as at least 2 percent by weight, or, in some cases, at least 3 percent by weight, with the weight percents being based on the total weight of the composition. In certain embodiments, the synthetic hectorite clay is present in the composition used in the methods of the present invention in an amount of no more than 10 percent by weight, such as no more than 6 percent by weight, or, in some cases, no more than 5 percent by weight, with the weight percents being based on the total weight of the composition.

[0016] In certain embodiments, the composition used in the methods of the present invention further comprises a source of chloride ions. The presence of a source of chloride ions can be particularly beneficial when the removal of mill scale is required or desired. Suitable chloride sources include, for example, hydrochloric acid, calcium chloride, sodium chloride, ammonium chloride, and potassium chloride, among many others.

[0017] In certain embodiments, the chloride source is present in the composition used in the methods of the present invention in an amount of at least 1 percent by weight, such as at least 2 percent by weight, or, in some cases, at least 3 percent by weight, with the weight percents being based on the total weight of the composition. In certain embodiments, the chloride source is present in the composition used in the methods of the present invention in an amount of no more than 10 percent by weight, such as no more than 8 percent by weight, or, in some
cases, no more than 6 percent by weight, with the weight percents being based on the
total weight of the composition.

[0018] In certain embodiments, the composition used in the methods of the
present invention further comprises an organic solvent, such as a water miscible
organic solvent. Suitable such solvents include monoalkyl or dialkyl ethers of
ethylene glycol or diethylene glycol, or a mono-, di-, or trialkyl ether of triethylene
glycol and the acetate derivatives thereof. The alkyl group often ranges from 1 to 4
carbon atoms. Suitable examples are saturated glycols containing at least four carbon
atoms or a compound containing Formula I:

\[
\text{R} \overset{\text{O}}{\text{CH}_2\text{R}_1} \overset{\text{O-H}}{\text{n}} \text{R}_2
\]

in which: R is independently selected from the group consisting of hydrogen, alkyl of
from 1 to 4 carbon atoms and -(O)C–CH₃; R₁ is independently selected from the
group consisting of -CH₂, -CH₂–CH–, -CH₂–CH(CH₃)–, and -CH(CH₃OH)–; R₂ is
independently selected from the group consisting of alkyl of from 1 to 4 carbon
atoms, hydroxyl substituted alkyl of from 1 to 4 carbon atoms and -(O)C–CH₃.

[0019] Exemplary solvents are Cellosolve (trademark for monoethyl ether of
ethylene glycol), methyl Cellosolve, butyl Cellosolve, isobutyl Cellosolve, hexyl
Cellosolve, Carbitol (trademark for monoethyl ether of diethylene glycol), butyl
Carbitol, hexyl Carbitol, monobutyl ether of propylene glycol, monopropyl ether of
propylene glycol, monomethyl ether of propylene glycol, monomethyl ether of
dipropylene glycol, butoxytriglycol C₄H₉O(C₂H₄–O)₃H, methoxytriglycol
CH₃O(C₂H₄–O)₃H, ethoxytriglycol C₂H₅O(C₂H₄O)₃H, 1-butoxyethoxy-2-propanol,
diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol,
tripropylene glycol, polypropylene glycol, having a molecular
weight up to 2000, hexylene glycol, 2 ethyl-1,3-hexane diol; 1,5-pentane diol, ester
diol-204 (2,2-dimethyl-3-hydroxypropyl 2,2-dimethyl-3-hydroxy propionate), and
the like.

[0020] Suitable water miscible alcohols that may be employed in the present
invention have from 1 to 8 carbon atoms, such as methanol, ethanol, propanol,
butanol, isobutanol, pentanol, hexanol, heptanol, octanol, methylamyl alcohol and the
like.
Suitable water miscible aliphatic ketones that may be employed in the present invention are acetone, methyl ethyl ketone, diethyl ketone, methyl propyl ketone, methyl isobutyl ketone, methoxy acetone, cyclohexanone, methyl n-amyl ketone, methyl isoamyl ketone, ethyl butyl ketone, disisobutyl ketone, isophorone, acetyl acetone (2,4-pentane dione), diacetone alcohol (CH₃)₂C(OH)CH₂C(O)CH₃.

In certain embodiments, the organic solvent is present in the composition used in the methods of the present invention in an amount of at least 1 percent by weight, such as at least 2 percent by weight, or, in some cases, at least 3 percent by weight, with the weight percents being based on the total weight of the composition. In certain embodiments, the chloride source is present in the composition used in the methods of the present invention in an amount of no more than 10 percent by weight, such as no more than 8 percent by weight, or, in some cases, no more than 6 percent by weight, with the weight percents being based on the total weight of the composition.

The compositions used in the methods of the present invention may also comprise any of a variety of optional ingredients, such as colorants, surfactants, corrosion inhibitors, preservatives, fillers, abrasives, buffers, fragrances, and the like.

The remainder of the composition used in the methods of the present invention is typically water, such as, for example, deionized water.

In certain embodiments, the compositions used in the methods of the present invention are substantially free, or completely free, of strong acids that produce a by-product that is environmentally undesirable, such as phosphoric acid and/or sulfuric acid. As used herein, “substantially free” when used with reference to the absence of a strong acid in the compositions described herein means that the composition includes less than 1% by weight, such as less than 0.1 % by weight, of the strong acid. As used herein, “completely free” means that there is no strong acid in the composition at all.

In certain embodiments, the composition used in the methods of the present invention has a low shear viscosity (As used herein, “low shear viscosity” refers to a viscosity measured on a Physica MCR301 viscometer with a CP50-1/TG spindle for 70 seconds at a shear rate of 0.01s⁻¹ and at 23°C. of at least 1,000 Pa·s, such as at least 2,000 Pa·s, or, in some cases, at least 4,000 Pa·s or at least 5,000 Pa·s. In certain embodiments, the composition used in the methods of the present invention has a high shear viscosity (As used herein, “high shear viscosity” refers to a viscosity
measured on a Physica MCR301 viscometer with a CP50-1/TG spindle at a shear rate of \(10^{4}\) s\(^{-1}\) for 5 seconds at 23°C.) of no more than 0.50 Pa·s, such as no more than 0.1 Pa·s, or, in some cases, no more than 0.01 Pa·s.

[0027] In certain embodiments, the composition used in the methods of the present invention has a pH of no more than 6.0, such as 2.0 to 5.0, or, in some cases, 3.0 to 4.0.

[0028] In the methods of the present invention, the composition is contacted with the metal containing surface by any of a variety of methods, such as by brushing, spraying, or dipping, among many other methods. The compositions described herein are particularly suitable for spray application using conventional pressure pot equipment or HVLP equipment. Because of the thixotropic nature of the compositions described herein, the methods of the present invention can be suitable for use with substantially vertically oriented ferrous metal-containing surface, such as can be the case with, for example, large structures, such as storage tanks, bridges, ships and other vehicles, among many others.

[0029] Once applied the composition is allowed to remain on the metal containing surface to remove rust to the extent desired or required. Contact time often ranges from at least 5 minutes to several hours, often at least 30 minutes, in some cases at least 3 or 4 hours, depending on the severity of the rust and the temperature at which the cleaning is conducted. The derusted surface may then be washed with water to remove the composition described herein, the loosened rust and dissolved rust. In some cases, more than one application of the composition described herein may be desired. Mechanically removing loose rust and scale, by wire brushing for example, prior to application of the composition described herein, may also be desired.

[0030] The present invention also relates to, *inter alia*, metal surfaces treated by the methods of the present invention.

[0031] Illustrating the invention are the following examples that are not to be considered as limiting the invention to their details. All parts and percentages in the examples, as well as throughout the specification, are by weight unless otherwise indicated.

**EXAMPLE 1**

[0032] Five solutions were prepared using the ingredients and amounts (in grams) listed in Table 1. Rusted panels were prepared by cleaning 3x4 inch bare cold
rolled steel panels (available from ACT Test Panels LLC 273 Industrial Dr. Hillsdale, MI 49242) with a commercially available alkaline cleaner (CK2010 commercially available from PPG Industries, Inc.) and then placing the panels in a salt spray chamber for four hours. The panels were rinsed with de-ionized water and allowed to air dry under ambient conditions prior to application of the solutions.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Example 1A</th>
<th>Example 1B</th>
<th>Example 1C</th>
<th>Example 1D</th>
<th>Example 1E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laponite RD(^1)</td>
<td>6</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Klucel M(^2)</td>
<td>--</td>
<td>1.5</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Klucel H(^3)</td>
<td>--</td>
<td>--</td>
<td>1.5</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Polyvinylpyrrolidone(^4)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>15</td>
<td>--</td>
</tr>
<tr>
<td>Gelatin (Calf Skin)(^5)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>15</td>
</tr>
<tr>
<td>Deionized water</td>
<td>114</td>
<td>118.5</td>
<td>118.5</td>
<td>105</td>
<td>105</td>
</tr>
<tr>
<td>Citric acid</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

\(^1\) Laponite RD is commercially available from Southern Clay Products, Inc. In Example 1A, the Laponite RD was incorporated into the water following the manufacturer’s recommendations. The citric acid was then slowly added while stirring the solution.

\(^2\) Klucel M is a hydroxyl propyl cellulose (M\(_w\) of about 850,000) available from Hercules Inc. In Example 1B, the Klucel M material was sifted into the water while stirring. After the material had dissolved, the citric acid was slowly added while stirring.

\(^3\) Klucel H is a hydroxyl propyl cellulose (M\(_w\) of about 1,150,000) available from Hercules Inc. In Example 1C, the Klucel H material was sifted into the water while stirring. After the material had dissolved, the citric acid was slowly added while stirring.

\(^4\) The polyvinylpyrrolidone, commercially available from Sigma-Aldrich Co., had an average M\(_w\) of about 1,300,000. In Example 1D, the polyvinylpyrrolidone was sifted into the water while stirring. After the material had dissolved, the citric acid was slowly added while stirring.

\(^5\) The gelatin is commercially available from Sigma-Aldrich Co. In Example 1E, the gelatin was sifted into the water while stirring. After the material had dissolved, the citric acid was slowly added while stirring.
Test Substrates

[0033] A portion of each of the above solutions were applied via a pipette onto a set of rusty steel panels that were disposed at an angle of approximately 80° from horizontal. After two hours, the panels were rinsed with deionized water and examined for approximate percentage of rust removed. The results are in Table 2.

<table>
<thead>
<tr>
<th>Example</th>
<th>Approximate % of rust removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>100</td>
</tr>
<tr>
<td>1B</td>
<td>80</td>
</tr>
<tr>
<td>1C</td>
<td>90</td>
</tr>
<tr>
<td>1D</td>
<td>50</td>
</tr>
<tr>
<td>1E</td>
<td>30</td>
</tr>
</tbody>
</table>

EXAMPLE 2

[0034] Three solutions were prepared using the ingredients and amounts (in grams) listed in Table 3. In each Example, the clay was sifted into the water while stirring. The Laponite RD containing material showed an increase in viscosity after a few minutes after incorporation. Within twenty minutes, the solution became clear with no visible particles. The Bentonite solution showed a very slight change in viscosity after addition to the water and the material remained an opaque, blue-green color. The Kaolin material did not show any change in viscosity after addition. After each clay was added, the solution was stirred for approximately 20 minutes, the citric acid was added and the resulting mixture was stirred for about 10 minutes.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Example 2A</th>
<th>Example 2B</th>
<th>Example 2C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized Water</td>
<td>380</td>
<td>380</td>
<td>380</td>
</tr>
<tr>
<td>Laponite RD$^1$</td>
<td>20</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Bentonite$^2$</td>
<td>--</td>
<td>20</td>
<td>--</td>
</tr>
<tr>
<td>Kaolin$^2$</td>
<td>--</td>
<td>--</td>
<td>20</td>
</tr>
<tr>
<td>Citric acid</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

$^1$ Commercially available from Southern Clay Products, Inc.

$^2$ Commercially available from VWR International, LLC.
Rusty panels were prepared as described in Example 1. The three solutions were spray applied using a garden sprayer to the panels which were disposed at an angle of approximately 80° from horizontal. After 1 hour, the panels were rinsed with water and the amount of rust removal was visually assessed. Approximately 100% of the rust was removed with the solution of Example 2A, while neither Examples 2B and 2C showed any rust removal.

The rheology of the three solutions was measured using a Paar-Physica MCR 301 Rheometer with a CP50-1/TG spindle at various shear rates and at 23°C. Results are set forth in Table 4.

<table>
<thead>
<tr>
<th>Shear rate (1/s)</th>
<th>Example 2A (Pa·s)</th>
<th>Example 2B (Pa·s)</th>
<th>Example 2C (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>5,040</td>
<td>35.8</td>
<td>8.92</td>
</tr>
<tr>
<td>0.1</td>
<td>457</td>
<td>4.65</td>
<td>1.03</td>
</tr>
<tr>
<td>1</td>
<td>54.2</td>
<td>0.551</td>
<td>0.115</td>
</tr>
<tr>
<td>10</td>
<td>4.42</td>
<td>0.0678</td>
<td>0.0295</td>
</tr>
<tr>
<td>100</td>
<td>0.319</td>
<td>0.0141</td>
<td>0.00693</td>
</tr>
<tr>
<td>1000</td>
<td>0.0683</td>
<td>0.00641</td>
<td>0.00328</td>
</tr>
</tbody>
</table>

Three solutions were prepared containing the same theoretical amounts of chloride using the ingredients and amounts (in grams) listed in Table 5. In each case the Laponite RD was incorporated into the water following the manufacturer’s recommendations. The citric acid was then slowly added while stirring the solution. For Example 3A, the hydrochloric acid was then added drop wise while stirring. For Example 3B, the sodium chloride was then added while stirring. For Example 3C, the ammonium chloride was then added while stirring.
<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Example 3A</th>
<th>Example 3B</th>
<th>Example 3C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>317.5</td>
<td>342.9</td>
<td>346.1</td>
</tr>
<tr>
<td>Laponite RD</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Citric acid</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>37% HCl*</td>
<td>62.5</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>NaCl*</td>
<td>--</td>
<td>37.1</td>
<td>--</td>
</tr>
<tr>
<td>NH₄Cl*</td>
<td>--</td>
<td>--</td>
<td>33.9</td>
</tr>
</tbody>
</table>

*Commercially available from VWR International, LLC.

[0038] Rusty panels were prepared as in Example 1. The three solutions were applied to the panels disposed at an angle of approximately 80° from horizontal. After 1 hour, the panels were rinsed with water and the amount of rust removal was visually assessed. Approximately 100% of the rust was removed with all three solutions.

**EXAMPLE 4**

[0039] Three solutions were prepared containing the same theoretical amounts of carboxylic acid containing compound using the ingredients and amounts (in grams) listed in Table 6. In each case the Laponite RD was incorporated into the water following the manufacturer’s recommendations. The acid was then slowly added while stirring the solution.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Example 4A</th>
<th>Example 4B</th>
<th>Example 4C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>106.5</td>
<td>106.5</td>
<td>116</td>
</tr>
<tr>
<td>Laponite RD</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Lactic acid (80% in H₂O)*</td>
<td>37.5</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Tartaric acid (80% in H₂O)*</td>
<td>--</td>
<td>37.5</td>
<td>--</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>--</td>
<td>--</td>
<td>30</td>
</tr>
</tbody>
</table>

*Commercially available from VWR International, LLC.

[0040] Rusty panels were prepared as in Example 1. The three solutions were applied to the panels disposed at an angle of approximately 80° from horizontal. After 1 hour, the panels were rinsed with water and the amount of rust removal was
visually assessed. Approximately 100% of the rust was removed with all three solutions.

[0041] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications which are within the spirit and scope of the invention, as defined by the appended claims.
WE CLAIM:

1. A method for removing rust from a ferrous metal-containing surface comprising contacting the surface with a composition comprising:
   (a) a carboxylic acid;
   (b) a synthetic hectorite clay; and
   (c) water.

2. A ferrous metal-containing surface treated by the method of claim 1.

3. The method of claim 1, wherein the rust comprises an iron oxide and/or iron hydroxide.

4. The method of claim 1, wherein the ferrous metal comprises steel.

5. The method of claim 1, wherein the steel comprises mild steel.

6. The method of claim 1, wherein the carboxylic acid comprises an aliphatic hydroxy acid.

7. The method of claim 6, wherein the aliphatic hydroxyl acid comprises citric acid.

8. The method of claim 1, wherein the carboxylic acid is present in the composition in an amount of at least 10 percent by weight and no more than 30 percent by weight, based on the total weight of the composition.

9. The method of claim 1, wherein the synthetic hectorite clay has the chemical formula NaO_5(Mg, Li)_3Si_4O_10(F,OH)_2.

10. The method of claim 1, wherein the average diameter of the synthetic hectorite is 1 to 30 nanometers.
11. The method of claim 1, wherein the synthetic hectorite clay is present in the composition in an amount of at least 1 percent by weight and no more than 10 percent by weight, based on the total weight of the composition.

12. The method of claim 1, wherein the composition further comprises a source of chloride ions.

13. The method of claim 1, wherein the composition has a low shear viscosity of at least 1,000 Pa·s and a high shear viscosity of no more than 0.50 Pa·s.

14. The method of claim 13, wherein the composition has a low shear viscosity of at least 4,000 Pa·s and a high shear viscosity of no more than 0.01 Pa·s.

15. The method of claim 1, wherein the composition has a pH of no more than 6.0.

16. The method of claim 1, wherein the contacting comprises spraying the composition onto the metal containing surface.

17. The method of claim 17, wherein the ferrous-metal containing surface is oriented substantially vertically.

18. A method for removing rust from a ferrous metal-containing surface comprising spray applying a composition onto at least a portion of the ferrous metal-containing surface, the composition comprising:
   (a) a carboxylic acid;
   (b) a synthetic hectorite clay; and
   (c) water,

   wherein (i) the ferrous metal-containing surface is oriented substantially vertically, and (ii) the composition has a low shear viscosity of at least 1,000 Pa·s and a high shear viscosity of no more than 0.50 Pa·s.

19. The method of claim 18, wherein the composition further comprises a source of chloride ions.
20. The method of claim 18, wherein the carboxylic acid comprises citric acid.