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PERMANGANATE SILICATE CLEANER

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ABSTRACT OF THE DISCLOSURE

Compositions consisting of an alkali metal permanganate and alkali metal silicate which, when dissolved in aqueous solution, provide improved solutions for treating ferrous metal surfaces to remove scale deposits and other contaminants in the form of smut formed ~~thereon; particularly for the removal of oxide~~ incrustations and smut from ferrous metal surfaces which have been previously heat treated.

During fabrication and forming of ferrous metal articles, lubricants are employed to facilitate these operations. These lubricants which are deposited on the metal surface usually consist of various types of mineral and vegetable oils and heavy metal soaps.

Should the metal surface be heat treated, the residue deposited on the metal surface, is in part, oxidized and decomposed so that a surface film of oxide scale is formed. This tightly adherent heat scale must be removed from all portions of the metal surface so that it does not interfere with future processing of the workpiece.

Some portions of the oil residue and any dirt, which the metal surface tends to pick up during the processing operation, will remain on the surface as a difficult to remove deposit normally referred to as smut. This smut can be in the form of carbonaceous materials and decomposed greasy deposits. The smut is difficult to remove with conventional alkaline agents and acid pickling baths.

Current practice in the art, to remove such impurities and deposits from the metal surface, include a wide variety of cleaning and pickling processing steps such as alkaline cleaning, pickling, and water rinsing. A typical example of a commonly employed process would include the following treating steps: (1) harsh alkaline cleaning to remove loose soil, (2) water rinse, (3) acid pickling operation to secure preliminary scale attack, (4) water rinse, (5) treatment with permanganate-caustic soda solution, (6) water rinse, (7) acid pickling operation to remove any remaining residues.

Various mechanical operations such as wire brushing and sand blasting are also employed in the art in order to remove the heat scale and smut deposits.

A variety of alkaline cleaning solutions have been employed in the art to treat the surface after preliminary scale attack by the acid pickling bath, in order to effect removal of the heat scale and smut deposits on the surface. Particularly, an aqueous alkali solution containing an alkali metal hydroxide and an alkali metal permanganate is employed. The use of treating solutions consisting of permanganate and caustic soda have created handling problems and the necessity for close control of constituent concentrations. The use of permanganate and caustic soda in aqueous solution will cause the release of corrosive and irritating fumes which make supervision of the bath difficult.

This invention provides for compositions, for use in aqueous solutions to remove heat scale and smut deposits on the metal surface, so as to prepare the metal surface for subsequent treatment such as conversion coating, electroless copper coating prior to drawing, or further

fabrication. The compositions of this invention, when dissolved in water, yield treating solutions which provide for a minimum amount of treating time of the metal surface and for minimal equipment maintenance during operation of the process in which it is employed. This invention is particularly useful in cleaning ferrous metal surfaces which have been annealed and have deposited thereon burnt-in scale deposits. The dry composition suitable in the practice of the present invention consists essentially of an admixture of alkali metal permanganate and alkali metal silicate.

Another aspect of this invention provides for aqueous solutions which, consist essentially of an alkali metal permanganate, an alkali metal silicate, and water. By employing the aqueous solution of the present invention, in certain cases, the prior alkaline cleaning step employed in the art to remove loose dirt and the first pickling step employed to secure preliminary scale attack can be eliminated from the cleaning sequence.

The principal object of the present invention is to provide compositions, solutions and a cleaning process for removing the foreign matter and scale deposits on metal surfaces, in order to provide a clean surface suitable for subsequent finishing or fabricating treatments, such as conversion coating and drawing.

A particular object of this invention is to provide compositions and solutions for effectively removing annealing scale and smut deposits from ferrous metal surfaces.

A concomitant object of this invention is to provide novel cleaning compositions which can be easily handled and packaged and can be used in aqueous solution for removing heat scale and smut from ferrous metal surfaces.

An additional object of this invention is to provide a method for removing heat scale, smut and the like from ferrous metal rod and wire, wherein the treated metal surface is so conditioned that further surface treatment can be easily performed.

A more particular object of this invention is to decrease the time of treatment necessary to remove annealing scale and smut from ferrous metal surfaces.

These objects are accomplished by employing a dry composition comprising an alkali metal permanganate and an alkali metal silicate to prepare an aqueous solution, and employing said aqueous solution by the methods hereinafter provided.

The present invention is based upon the surprising discovery that a composition consisting of an alkali metal permanganate and an alkali metal silicate, when added to water, will form an aqueous alkaline solution which will effectively clean a metal surface which has been previously subjected to high temperatures so that a residue comprised of oxides, dirt and smut has been formed thereon. The alkali permanganate and alkali silicate bath is particularly effective for rendering heat scale and smut, which is formed during heat treating more readily removable.

The smut deposits and heat scale on the metal surface, and its particular form, depend on the compositions of the oils and other organic materials and inorganic materials which have been employed in the prior treatment of the metal surface, the composition of the particular metal surface being treated, and the conditions employed during heat treating.

The term "heat scale" used herein means deposits formed on the metal surface during heat treatment of the ferrous metal, which can include the products of the combustion of carbon and various types of oils and fats, as well as metal oxide resulting from oxygen combining with the metal at high temperatures. Particularly, the term "annealing scale" means that scale formed as the products of combustion during an annealing process. The term

"smut" used herein means a dark black residue deposited on the metal surface. The distinction between the heat scale and the smut deposits on the surface is that the scale can be subjected to attack by an acid pickle bath while the smut is a film of carbonaceous material, which is not subject to attack by an acid pickle bath.

It should be understood that the term "ferrous metal surface" used herein includes a wide variety of steels, iron and iron alloys, including alloys of iron with chromium and/or nickel.

The suitable alkali metal permanganates which are employed in the present invention are the permanganates of sodium and potassium. Preferably, potassium permanganate should be employed in the compositions of the present invention.

It will be appreciated that the alkali metal silicates to be employed in the present invention include the silicates of sodium, potassium, lithium, cesium and rubidium. The preferred alkali metal silicates for use in the present invention are potassium and sodium silicates.

The addition of the alkali silicate to the solutions of the present invention increases the detergency of the solution rendering it more effective in removing the smut deposits from the ferrous metal surface. The silicate is an excellent saponifying agent for the residual oils, fats and loose dirt on the surface.

The alkali silicate dissolved in water provides alkalinity to the bath. The alkali silicate in the aqueous solution of this invention maintains an almost constant and rather high pH. As the alkalinity of the solution is used up, these silicate salts have the property of liberating additional alkalinity and will maintain a relatively uniform hydroxyl ion concentration for long periods of time. So, the advantages of the present invention include not only the improved cleaning results with the use of the aqueous solution but also the beneficial properties of pH maintenance and stability of the solution during operation.

Typical examples of the alkali metal silicates which can be employed in the composition and aqueous solutions of the present invention are sodium metasilicate, sodium sesquisilicate and sodium orthosilicate. In the preferred practice of the present invention, anhydrous sodium orthosilicate should be employed in the aqueous metal treating solution.

A particular advantage of utilizing sodium orthosilicate is that it can be mixed with the dry alkali metal permanganate and can be stored without caking or lumping for long periods of time. The sodium orthosilicate is easily dissolved in water without the liberation of irritating fumes and it offers the properties of high alkalinity and good detergency.

The use of the aqueous solution of the present invention permits easy removal of smut formed on the metal surface during subsequent treating steps such as an acid pickling step.

In the acid pickling step, an acid bath is employed consisting of a mineral acid selected from the group of hydrochloric acid and sulfuric acid. A distinct advantage of the present invention is that a pickling operation prior to treatment with the solution of the present invention may not be necessary, depending on the particular ferrous metal alloys being treated.

The relative amounts of alkali metal silicate and alkali metal permanganate in the dry composition, expressed as a weight ratio, can be from ½ part by weight of alkali silicate for each part by weight of alkali permanganate and can be as much as 3 parts by weight of alkali silicate for each part by weight of alkali permanganate. Preferably, the dry composition should consist of 2 parts by weight of alkali metal silicate for each part by weight of alkali metal permanganate.

When the cleaning bath is initially prepared, the dry admixture composition should be added to water in sufficient amounts to produce a cleaning solution consisting of from about 20 grams/liter to about 100 grams/liter of alkali metal permanganate and from about 40 grams/liter to about 160 grams/liter of alkali metal silicate. It is recommended that in the preferred practice of this invention the aqueous solution comprises about 40 grams/liter of alkali metal permanganate and about 80 grams/liter of alkali metal silicate. It should be understood that greater or somewhat smaller amounts of the constituents can be used in the solution. Suffice it to say that the amount of permanganate and silicate in the solution should be an amount such that the desired improvements and results are realized.

The dry alkali silicate and alkali permanganate can be added separately to water to make up the cleaning solution of the present invention. However, it is preferred that the constituents be added as a dry admixture to sufficient amounts of water to make a solution with constituent concentrations within the limits specified herein.

The aqueous cleaning solution of the present invention should be replenished during operation of the process. The cleaning solution will become depleted in its constituents due to factors such as drag-out, and the action of the constituents on the heat scale and smut. For example, the permanganate will be reduced to MnO_2 and the silicate will be expended during its saponifying and detergent action. Simple titration methods known to the art can be employed in order to determine the concentrations of permanganate and silicate in the cleaning bath. For example, the permanganate concentration can be determined by acidifying the bath sample with sulfuric acid followed by titration with oxalic acid to a colorless endpoint.

It is within the purview of this invention to incorporate small amounts of a wetting agent into the aqueous cleaning solution so as to insure complete contact of the surface with the solution. The choice of wetting agent should be anionic in nature. Typical examples of wetting agents which can be employed are:

Du Pont's "Alkanol" B, sodium alkyl naphthalene sulfonate;

Du Pont's "Alkanol" DW, alkyl-aryl sodium sulfonate;

Monsanto's "Santomerse" 1, alkyl-aryl sodium sulfonate; and

Atlantic's "Ultra-Wet" K, alkyl benzene sodium sulfonate.

Prior to treatment with the aqueous solution of the present invention, the metal surface can be treated with an acid pickle bath. The pickle baths employed in the cleaning process specified herein form no part of the present invention and will have been applied using commonly employed processes and techniques known to the art. Particularly, the acid pickle baths employed prior to and after the application of the aqueous solution of the present invention can be comprised of a mineral acid selected from the group consisting of sulfuric acid and hydrochloric acid. In addition, the pickle bath can be preceded by an alkaline cleaning bath and water rinse to remove loose dirt from the metal surface.

In some cases, when the solution of the present invention is employed, it is not necessary that the surface undergo either a prior cleaning or pickling step or be subjected to any other preliminary treatment prior to contact with the aqueous solution of this invention. Should the metal surface be subjected to a pickle bath prior to application of the solution of the present invention, at least one intervening water rinse will be required after pickling and prior to treatment with the solution of the present invention.

Subsequent to the cleaning procedure of the present invention, the metal surface is usually subjected to a water rinse followed by acid pickling. The purpose for this subsequent pickling step is to remove any manganese dioxide deposited on the surface.

When the annealing scale that has deposited on the metal surface proves particularly difficult to remove employing the usual processing steps, it may be necessary to apply the aqueous solution of this invention to the surface on two separate occasions. In each case, treatment with the solution of this invention would be followed by an acid

pickling step and intervening water rinses. For example, the following processing steps could be effected: (1) treat with aqueous solution of the present invention, (2) water rinse, (3) acid pickling bath, (4) water rinse, (5) treat with aqueous solution of this invention, (6) water rinse, (7) acid pickling bath, and (8) water rinse.

In the process of the present invention, the workpiece is brought into contact with the aqueous solution under suitable conditions of temperature, pH and contact time. Contact can be effected by either immersion, spraying or flow-coating to produce the desired results. Preferably, the workpiece will be immersed in the aqueous solution.

The solution of the present invention should be operated at a pH above 12.0. Preferably, the cleaning process should be effected with a solution having a pH of from about 12.0 to about 13.5. The pH of the cleaning solution should not be allowed to fall below 12.0, since the solution will not be as effective in attacking and loosening the oxide scale and smut.

The aqueous solution of the present invention can be operated at temperatures as high as 212° F. It is preferred that the process of the present invention be operated at a temperature between about 150° to about 200° F. An important improvement of the present invention is the absence of deleterious and noxious fumes which do not evolve from the solutions during operation. In commercial practice, this is a great advantage allowing for easy maintenance of the working bath.

A distinct advantage of the present invention is the time of treatment required for effective removal of the oxide scale and smut deposits on the surface. I have found that by the use of the aqueous solution of the present invention the surface should be immersed, sprayed, or flow-coated, for a time from about 3 minutes to about 20 minutes. Preferably, the surface will be in contact with the aqueous solution for from about 4 minutes to 8 minutes.

The following examples are illustrative of this invention and are not considered as limiting for other materials and operating conditions falling within the scope of this invention that might be substituted.

EXAMPLE 1

Steel rod, ⅜" in diameter, was employed as the test material in this procedure. The steel rod was type 1038 alloy. The rod had been subjected to annealing heat treatment conditions and was covered with annealing scale and smut deposits.

The test specimens were treated as follows:

(1) Pickle at 170° F. for 10 minutes in 12% by volume sulfuric acid.
(2) Rinsed with water at ambient temperature.
(3) Immersed in aqueous solution consisting of potassium permanganate, sodium orthosilicate, and water, for 7 minutes at 170° F.
(4) Rinsed with water at ambient temperature.
(5) Pickle at 170° F. for 5 minutes in 12% by volume sulfuric acid.
(6) Rinsed with water at ambient temperature.
(7) Air dried.

The pickling baths employed in Steps 1 and 5 may, if desired, contain a coal tar base inhibitor to give them the property of dissolving the scale without substantially attacking the underlying metal surface.

In Step 3, the steel rods were subjected to aqueous solutions falling within the purview of this invention. Each cleaning solution employed herein was prepared by adding a dry admixture consisting of potassium permanganate and anhydrous sodium orthosilicate to water. The concentration and relative amounts of these constituents in the solution was varied for each traverse as illustrated in Table 1.

For purposes of comparison, one group of control test specimens was treated exactly the same way, except for Step 3 wherein treatment was effected with an aqueous cleaning solution consisting of 120 grams/liter of sodium hydroxide and 60 grams/liter of potassium permanganate.

The results reported in Table 1 represent observations made to determine the presence of smut on the surface after processing was completed and the brightness appearance of the test specimens at the end of the processing procedure.

The brightness quality was determined by visually rating the degree of brightness of the surface. A brightness rating of 1 represents best performance and appearance and a rating of 4 represents poor appearance.

The presence of smut on the surface was determined by rubbing the surface with a clean white cloth and observing the smut deposited on the cloth. The presence of smut is evidenced by a dark black residue on the white cloth. The amount of smut present is expressed in graduations from very light to heavy smut.

A comparison or results of the various treatments is presented in Table 1.

TABLE 1

Aqueous cleaning solution			
Amount of dry admixture per liter of water	Wt. ratio in dry admixture	Presence of smut	Brightness
Grams per liter:			
100	2 parts by wt. sodium orthosilicate/3 parts by wt. potassium permanganate.	Very light	1
120	1 part by wt. sodium orthosilicate/1 part by wt. potassium permanganate.	No smut	1
140	4 parts by wt. sodium orthosilicate/3 parts by wt. potassium permanganate.	do	1
160	5 parts by wt. sodium orthosilicate/3 parts by wt. potassium permanganate.	do	1
180	2 parts by wt. sodium orthosilicate/1 part by wt. potassium permanganate.	do	1
200	7 parts by wt. sodium orthosilicate/3 parts by wt. potassium permanganate.	do	1
220	8 parts by wt. sodium orthosilicate/3 parts by wt. potassium permanganate.	do	1
Control		Moderate smut deposit.	

EXAMPLE 2

Cold-rolled cylindrical steel articles, which had been subjected to annealing treatment, were employed in this test procedure. The test specimens were comprised of various steel alloys. The articles were covered with heat scale and smut deposits.

The following sequence of treating steps was effected:

(1) Pickle at 170° F. for 10 minutes in 12% by volume sulfuric acid.
(2) Rinsed with water at ambient temperature.
(3) Immersed in aqueous solution consisting of potassium permanganate, sodium orthosilicate, and water, for 7 minutes at 170° F.
(4) Rinsed with water at ambient temperature.
(5) Pickle at 170° F. for 5 minutes in 12% by volume sulfuric acid.

(6) Rinsed with water at ambient temperature.
(7) Air dried.

The pickling solutions employed in Steps 1 and 5 may, if desired, contain a coal tar base inhibitor in order to prevent vigorous attack of the underlying metal surface.

The aqueous alkaline solution within the scope of this invention, and employed in Step 3, was prepared by the addition to water of a dry composition comprising an admixture of potassium permanganate and anhydrous sodium orthosilicate. For each part by weight of potassium permanganate there was 2 parts by weight of sodium orthosilicate in said composition. 180 grams of the composition was added to each liter of water, such that the aqueous solution was comprised of 120 grams/liter of sodium orthosilicate and 60 grams/liter of potassium permanganate.

For purposes of comparison, cylindrical steel articles of the various alloys were subjected to a similar test procedure except that they were treated with an aqueous alkaline solution comprised of 120 grams/liter of sodium hydroxide and 60 grams/liter of potassium permanganate in Step 3 of the process.

The results reported in Table 2 represent the determination of the amount of smut which remained on the surface after the test procedure had been effected and an indication of the extent of scale removal accomplished based upon the brightness exhibited by the test specimens.

The brightness rating of each test article in Table 2 is based on visual observation and is expressed by a rating of 1 to 4, wherein 4 is the lowest rating and represents a metal surface with the most scale and smut remaining thereon.

The test articles were examined for any traces of smut by rubbing the surface with a clean white cloth. The presence of any smut was evidenced by a dark black residue on the white cloth. The amount of smut present is expressed in Table 2 as from very light to heavy smut.

The results in Table 2 illustrate the excellent results, in terms of heat scale removal and smut removal, obtained with the aqueous solutions of the present invention.

TABLE 2

Type of alloy treated	Aqueous solution	Brightness rating	Smut presence
1010	Potassium permanganate plus sodium orthosilicate.	1	No smut.
1018	do	1	Do.
1022	do	1	Do.
1030	do	1	Do.
1038	do	1	Do.
4037	do	1	Do.
8637	do	2	Light.
X-22-A	do	2	Do.
1010	Potassium permanganate plus sodium hydroxide.	1	No smut.
1018	do	1	Do.
1022	do	2	Light.
1030	do	1	No smut.
1038	do	3	Moderate.
4037	do	2	Light
8637	do	4	Heavy.
X-22-A	do	2	Light.

EXAMPLE 3

Steel rod, 3/8" in diameter, was employed as the test article in this procedure. The steel rod was type 1022 alloy. The metal rod had been subjected to annealing heat treatment and was covered with heat scale and smut deposits.

The articles were treated in the following manner:

(1) Pickle at 170° F. for 10 minutes in 12% by volume sulfuric acid.
(2) Rinsed with water at ambient temperature.
(3) Immersed in aqueous solution consisting of potassium permanganate, sodium orthosilicate, and water, for 7 minutes at 170° F.
(4) Rinsed with water at ambient temperature.
(5) Pickle at 170° F. for 5 minutes in 12% by volume sulfuric acid.
(6) Rinsed with water at ambient temperature.
(7) Air dried.

The sulfuric acid pickling baths employed in Steps 1 and 5 may, if desired, contain a coal tar base inhibitor to prevent vigorous attack of the underlying metal surface.

The treating solutions employed in Step 3 were prepared by adding to water a dry composition comprising an admixture consisting of anhydrous sodium orthosilicate and potassium permanganate. The amount of the dry composition added to water and the relative amounts of the constituents was varied for each traverse as illustrated in Table 3.

The results in Table 3 represent a determination of the amount of smut remaining on the surface after the workpiece was treated and a determination of the heat scale removed by qualitatively rating the surfaces by brightness and appearance.

The degree of brightness of each surface was rated from 1 to 4, wherein 1 represents the best performance and 4 represents a poor and dull appearance.

The presence of smut on the surface was determined by rubbing the test article with a clean white cloth and observing the smut deposited on the cloth. The presence of smut is evidenced by a dark black residue on the white cloth. The amount of smut remaining on the surface and deposited on the cloth is expressed from very light to heavy smut.

TABLE 3

Aqueous treating solution			
Amount of dry composition per liter of water	Wt. ratio in dry composition	Smut remaining	Brightness
Grams per liter:			
60	1 part by weight sodium orthosilicate/2 parts by weight potassium permanganate.	No Smut	1
80	1 part by weight sodium orthosilicate/1 part by weight potassium permanganate.	do	1
100	3 parts by weight sodium orthosilicate/2 parts by weight potassium permanganate.	do	1
120	2 parts by weight sodium orthosilicate/1 part by weight potassium permanganate.	do	1
160	3 parts by weight sodium orthosilicate/1 part by weight potassium permanganate.	do	1

EXAMPLE 4

Steel rod, 3/8" in diameter, of type 1022 alloy and 4037 alloy was employed in this procedure. The metal surface had been subjected to annealing heat treatment and was covered with heat scale and smut deposits.

The rod was treated in the following manner:

(1) Pickle at 170° F. for 10 minutes in 12% by volume sulfuric acid.
(2) Rinsed with water at ambient temperature.
(3) Immersed in aqueous solution consisting of alkali metal silicate, potassium permanganate, and water, for 7 minutes at 170° F.
(4) Rinsed with water at ambient temperature.
(5) Pickle at 170° F. for 5 minutes in 12% by volume sulfuric acid.
(6) Rinsed with water at ambient temperature.
(7) Air dried.

The sulfuric acid pickling solutions may, if desired, contain a coal tar base inhibitor to prevent vigorous attack of the underlying metal surface.

In Step 3, the workpieces were immersed in aqueous treating solutions within the scope of this invention. The treating solutions employed herein were prepared by adding a dry composition to water, said composition comprising an admixture of an alkali silicate and potassium permanganate. For each part by weight of potassium permanganate, there was two parts by weight of alkali metal silicate in the composition.

The results in Table 4 represent the determination of smut remaining on the surface and the degree of scale removal.

The brightness of the metal surfaces was observed as in the previous examples and rated accordingly. Likewise, the smut remaining on the surface was determined in the same manner as before.

TABLE 4

Aqueous treating solution				
Amount of dry compositions per liter of water	Constituents and their weight in ratio dry composition	Type alloy treated	Brightness	Smut present
Grams per liter.				
180	2 parts by weight sodium metasilicate (anhydrous)/1 part by weight potassium permanganate.	4037	1	Very light.
180	do	1022	1	Do.
180	2 parts by weight sodium sesquisilicate pentahydrate/1 part by weight potassium permanganate.	1022	1	No smut.

EXAMPLE 5

Steel rod, ⅜" in diameter, was employed in this procedure. The various alloys employed were type 1022, 1030, 1018 and 1038. The test articles had been subjected to annealing heat treatment and were covered with heat scale and smut deposits.

The articles were treated in the following manner:

(1) Immersed in aqueous solution consisting of potassium permanganate, sodium orthosilicate, and water, for 7 minutes at 170° F.
(2) Rinsed with water at ambient temperature.
(3) Pickled at 170° F. for 5 minutes in 12% by volume sulfuric acid.
(4) Rinsed with water at ambient temperature.
(5) Air dried.

The sulfuric acid pickling bath in Step 3 may, if desired, contain a coal tar base inhibitor so as to prevent vigorous attack of the underlying metal surface.

In Step 1, the test articles were immersed in an aqueous treating solution prepared by adding a dry composition consisting of potassium permanganate and anhydrous sodium orthosilicate to water. The dry composition contained 2 parts by weight of sodium orthosilicate for each part by weight of potassium permanganate. 180 grams of the composition was added per liter of water to prepare the treating solution.

In this procedure the test articles did not undergo a pickling treatment prior to treatment with the aqueous sodium orthosilicate-potassium permanganate solution. The results in Table 5 illustrate that smut and scale can be effectively removed without the necessity of a prior pickling step in some cases.

The results in Table 5 represent the determination of smut remaining on the surface and the degree of scale removal. The brightness was rated as in the previous tests and the smut remaining was determined in the same manner as hereinbefore.

TABLE 5

Type alloy treated	Brightness	Smut present
1018	1	Very light.
1022	1	No smut.
1030	1	Very light.
1038	1	Do.

I claim:

1. A solid composition, which when added to water forms an aqueous solution for treating ferrous metal surfaces, consisting essentially of an alkali metal silicate selected from the group consisting of alkali metal orthosilicate, alkali metal metasilicate, and alkali metal sesquesilicate, and an alkali metal permangnnate selected from the group consisting of sodium permanganate and potassium permanganate, wherein for each part by weight of alkali metal permanganate in said composition, there is from ½ part to 3 parts by weight of alkali metal silicate.

2. An aqueous solution for treating ferrous metal surfaces which consists essentially of: an alkali metal silicate selected from the group consisting of alkali metal orthosilicate, and alkali metal sesquesilicate; and an alkali metal permanganate selected from the group consisting of sodium permanganate and potassium permanganate.

3. A solution as in claim 2 wherein the alkali metal silicate is present in an amount between about 40 grams/liter and about 160 grams/liter and the alkali metal permanganate is present in an amount between about 20 grams/liter and about 100 grams/liter.

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