United States Patent Office

3,425,947
Patented Feb. 4, 1969

3,425,947

METHOD OF TREATING METAL SURFACES

Werner Rausch, Stierstadt, Taunus, and Gerhard Koch, Gottingen, Germany, assignors to Hooker Chemical Corporation, Niagara Falls, N.Y., a corporation of New York

No Drawing. Filed May 2, 1966, Ser. No. 546,613
U.S. Cl. 252—105 7 Claims
Int. Cl. C11d 7/02, 7/06, 7/10

ABSTRACT OF THE DISCLOSURE

An alkaline concentrate composition, useful in formulating alkaline treating solutions for removing organic impurities from ferrous metal surfaces which comprises an alkali metal hydroxide, an alkali metal permanganate, and an inorganic reducing agent, preferably selected from alkali metal sulfides, sulfites, bisulfites, pyrosulfites, phosphites and hypophosphites. The reducing agent is preferably present in an amount of about 1 gram equivalent of reducing agent per gram mole of the alkali metal permanganate.

This invention relates to a method for treating metal surfaces and more particularly relates to a method for treating metal surfaces so as to remove therefrom organic impurities.

In the treatment of metal surfaces to remove oil films, carbon films, lacquer coatings, etc., it has been known in the past first to subject the metal surfaces to a vapor degreasing operation, using for example, perchloroethylene or trichloroethylene vapors. Thereafter, the degreased surfaces are normally subjected to an acid pickle, to complete the removal of the coating from the metal. In many instances, it has been found that undesirably long pickling times are required when this process is used.

Accordingly, it has been proposed to substitute for the vapor degreasing process a dipping or immersion treatment, preferably at raised temperatures, in a concentrated aqueous alkali solution, such as sodium hydroxide or potassium hydroxide, which preferably also contains an alkaline permanganate. Such treatment baths typically contain from about 10 to 30% of a concentrate composition, which concentrate contains from about 10 to 50% of the permanganate, such as potassium permanganate and 90 to 50% of the alkali, such as potassium hydroxide or sodium hydroxide. Metal treating processes using these aqueous alkaline solutions have been found greatly to reduce the subsequent treating time in the acid pickle in most instances.

With these aqueous treating solutions, however, appreciable amounts of heat are evolved when the concentrate is dissolved in the water. Additionally, oxygen is formed in the solution according to the equation:

$$4KMnO_4+4KOH\rightarrow 4K_2MnO_4+2H_2O+O_2\uparrow$$

This gaseous oxygen escapes from the bath in very fine bubbles which carry along with them clouds of the alkaline, strongly oxidizing bath solution. These vapors are corrosive and irritate the eyes and mucous membranes and, hence, are very objectionable to personnel working in the vicinity of the baths. Thus, up to the present time, it has been possible to obtain the advantage in decreased processing time when using these baths only with the disadvantage of the evolution of these corrosive and irritating vapors.

It is, therefore, an object of the present invention to

provide an improved composition and method for removing organic material from metal surfaces.

A further object of the present invention is to provide an improved composition and method for removing organic materials from metal surfaces, which do not involve the evolution of noxious and harmful gases and vapors from the treating solution when used.

These and other objects of the invention will become apparent to those skilled in the art from the description which follows.

Pursuant to the above objects, the present invention includes a concentrate composition useful in formulating alkaline cleaning baths, which composition comprises an alkali metal hydroxide, an alkali metal permanganate and an inorganic reducing agent, which later material is desirbly present in an amount of about 1 gram-equivalent per gram mole of the alkali metal permanganate.

More specifically, the alkaline concentrate composition contains an alkali metal hydroxide in an amount within the range of about 90 to about 50% by weight of the composition and an alkali metal permanganate in an amount within the range of about 10 to about 50% by weight of the composition, with the reducing agent being present in an amount of about 1 gram equivalent of reducing agent per gram mole of the permanganate. In a preferred concentrate mixture, the components are present in the following amount:

Alkali metal hydroxide	gram moles	2–20
Alkali metal permanganate	do	1
Reducing agent	gram-equivalents	0.8–1

It is to be appreciated that the term "alkali metal" as used in the specification and claims is intended to refer to sodium, potassium, lithium, cesium and rubidium. Of these, the preferred alkali metals are sodium and potassium and, hence, hereinafter primary reference will be made to the compounds of these elements. Accordingly, the preferred alkali metal hydroxides for use in the present invention are potassium hydroxide and sodium hydroxide while the preferred alkali metal permanganates are potassium permanganate and sodium permanganate.

Various suitable inorganic reducing agents may be used in the composition of the present invention. These include metal salts as well as various sulfur and phosphorus compounds. Exemplary of metal salts which may be used are ferrous iron salts and stannous tin salts, while the alkali metal sulfides, and alkali metal salts of oxy-acids of sulfur, such as the alkali metal sulfites, bisulfites and pyrosulfites, and the alkali metal phosphites and hypophosphites are exemplary of the sulfur and phosphorus compounds which may be used. In some instances, it has been found that the ferrous iron salts produce a somewhat voluminous precipitate of ferric hydroxide which, may be disadvantageous. Additionally, although the stannous tin salts are not subject to this disability, their high cost is often a deterrent to their extensive use. Accordingly, the preferred reducing agents for use in the present invention are the anionic reducing agents, i.e., the alkali metal sulfur and phosphorus compounds, and in particular, the alkali metal sulfites, bisulfites and pyrosulfites. Additionally, however, in many instances, excellent results have also been obtained when using the alkali metal sulfides and alkali metal hypophosphites.

In formulating aqueous alkaline solutions for treating metal surfaces in accordance with the present invention, the alkaline concentrate compositions as have been described hereinabove are dissolved in water, desirably in

amounts within the range of about 5 to about 40% by weight of the concentrate composition. Preferably, these treating solutions contain from about 10 to about 30% by weight of the concentrate composition. Although the temperaure of the water used in formulating these treating solutions is not critical, it is generally preferred to use cold water in order to minimize the exothermic reaction when the concentrate is dissolved in water. It is found, that no noxious or health endangering vapors are formed either during the formulation of the treating solutions or during their use, so that special exhaust equipment is not required for the treating bath.

In addition to the concentrate composition as described hereinabove, the cleaning baths of the present invention may also contain other additives for enhancing the cleaning action, as are known to those in the art. For example, simple or complex fluorides may be added to the treating solution. These may be added as the acids, such as hydrofluoric acid, fluosilicic acid, fluoboric acid, or the like, or as the corresponding alkali metal salts of these acids. Typically, such additives may be present in the treating solution in amounts up to about 15% by weight of the treating solution, with amounts within the range of about 2 to about 6% by weight being preferred.

The cleaning solutions prepared as have been indicated hereinabove are preferably used at an elevated temperature, desirably at temperatures of about the boiling point of the solution. In this regard, temperatures within the range of about 85 to 100° centigrade are typical. Although lower bath temperatures may be used it has been found that in many instances, the contact time between the cleaning solution and the metal surface must be lengthened in order to obtain the same cleaning results as when using higher bath temperatures.

The cleaning solutions may be applied to the metal surface in any convenient manner, with dipping or immersion processes being preferred. In many instances, however, flow or spray processes may also be used. Obviously, the treatment times with the solutions of the present invention will depend upon the amount and nature of the impurities on the metal surfaces, although treatment times of up to about 15 to 20 minutes are typical and contact times of from about 1 to 10 minutes are preferred. In many instances, following the contact with the alkaline cleaning solutions of the present invention, the metal surfaces are then water rinsed and subjected to an acid pickling solution, utilizing aqueous solutions of hydrochloric acid, sulfuric acid, or the like, as are known in the art. In some instances, as for example where the metal surfaces contain complex mixtures of organic and oxide materials, the treatment with the cleaning solutions of the present invention may be interrupted, one or more times to treat the metal surface with an oxide dissolving solution, such as an aqueous hydrochloric or sulfuric acid pickling solution. In this manner, the total cleaning time may be reduced considerably, with a simultaneous improvement of the appearance of the metal surface.

It has been found that the treating solutions of the present invention may be advantageously used with many metals and alloys, including iron, steel, refined steel, chromium-nickel alloys, chromium-nickel-molybdenum alloys, nickel, nickel-copper alloys, nickel-molybdenum-iron alloys, and the like. Generally, however, it is not advisable to use these solutions on metals which are soluble in alkaline solutions, as for example, zinc, aluminum, or tin. The solutions of the present invention have been found to be effective in removing various organic materials from the metal surfaces, including oil carbon film, lacquer coatings, and the like.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. In these examples, unless otherwise indicated, temperatures are in degrees centigrade and percents and parts are by weight. It is to be appreciated, however, that these examples are merely exemplary of the present invention and are not to be taken as a limitation thereof.

Example 1

Three alkaline concentrate compositions were formulated containing the following components in the amounts indicated:

(A)

Component:	Percent
NaOH	67
$KMnO_4$	28
$Na_2S.9H_2O$	5

(B)

NaOH	67
$KMnO_4$	28
$NaH_2PO_2.H_2O$	5

(C)

NaOH	62.5
$KMnO_4$	26.8
Na_2SO_3	10.7

380 grams of each of the above concentrates were diluted with water to form a solution bath of 1 liter. In each instance, there was no evolution of corrosive or noxious vapors from the solution. The treating solutions were then heated to 100 degrees centigrade and hardened steel screws covered with oil carbon were dipped in the heated treating solution for 10 minutes and then rinsed with water for 10 minutes. Thereafter, the screws were pickled in a cold aqueous hydrochloric acid solution containing 15% hydrochloric acid. After the hydrochloric acid treatment, the screws had a bright metallic surface.

Example 2

The procedure of Example 1 was repeated with the exception that in place of the treatment in the alkaline cleaning solutions of Example 1, the screws were degreased in perchloroethylene vapor and pickled in the 15% hydrochloric acid solution. In this instance, it was found that a pickling time of 120 minutes was required before the surface of the screws was substantially free of the adhering oil carbon. Additionally, it was found that because of the long pickling time, deep pickling scars were formed on the metal surface, whereas the screws treated in Example 1 were completely free of pickling flaws.

Example 3

A series of three concentrate compositions were formulated as in Example 1 with the exception that in each of these compositions, the reducing agent was omitted. From 340 to 380 grams of these concentrate solutions were dissolved in water to make a total bath volume of 1 liter. In each instance, there was a strong evolution of noxious gases and fumes from the treating solutions. These fumes were extremely irritating to the eyes and mucous membranes of those in proximity to the solutions and required about 2 to 3 hours to dissipate.

While there have been described various embodiments of the invention, the methods and compositions described are not intended to be understood as limiting the scope of the invention, as it is realized that changes therewithin are possible and it is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. An alkaline concentrate composition, useful in formulating alkaline treating solution for removing organic impurities from ferrous metal surfaces, which concentrate composition consists essentially of from about 50 to 90% by weight of an alkali metal hydroxide, from about 10 to 50% by weight of an alkali metal permanganate and

about 1 gram-equivalent per mole of alkali metal permanganate of an inorganic reducing agent selected from alkali metal sulfides, sulfites, bisulfites, pyrosulfites, phosphites and hypophosphites.

2. The composition as claimed in claim 1 wherein the composition contains from about 2–20 gram moles of alkali metal hydroxide, one gram mole of alkali metal permanganate and about 0.8 to 1 gram equivalent of the reducing agent.

3. An aqueous alkaline solution useful in removing organic impurities from metal surfaces which comprises water and from about 5 to about 40% by weight of the alkaline concentrate composition of claim 1.

4. The alkaline treating solution as claimed in claim 3 wherein the alkaline concentrate composition used contains from about 2–20 gram moles of alkali metal hydroxide, 1 gram mole of alkali metal permanganate and 0.8 to 1 gram equivalent of the reducing agent.

5. A process for removing organic impurities from ferrous metal surfaces which comprises contacting the ferrous metal surface with the aqueous alkaline treating solution as claimed in claim 4 and maintaining the solution

in contact with the surface for a period sufficient to effect substantial removal of the organic impurities.

6. The process as claimed in claim 5 wherein in the aqueous treating solution used, the alkaline concentrate composition contains from about 2–20 gram moles of alkali metal hydroxide, about one gram mole of alkali metal permanganate and from about 0.8 to about 1 gram equivalent of reducing agent.

7. The process as claimed in claim 6 wherein the alkali metal hydroxide is sodium hydroxide, the alkali metal permanganate is potassium permanganate and the reducing agent is sodium sulfite.

References Cited

UNITED STATES PATENTS

3,216,857 11/1965 Du Vall ---------- 134—39 XR

MAYER WEINBLATT, *Primary Examiner.*

U.S. Cl. X.R.

252—103, 79.5, 188; 134—2, 38, 39, 40