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3,025,189

**COMPOSITION AND PROCESS FOR REMOVING  
HEAT SCALE FROM METAL PARTS**

Benjamin Arden, Portuguese Bend, Calif., assignor, by  
mesne assignments, to Purex Corporation, Ltd., a cor-  
poration of California

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This invention relates to removal of deposits on metal parts. A particularly important application of my invention is the removal of heat scale or oxide scale formed at high temperatures, from metal parts, e.g. austenitic stainless steels such as the chromium-nickel stainless steels, nickel base alloys, cobalt base alloys and the so-called super alloys and heat resistant alloys generally. This invention is concerned with novel procedure and compositions for the removal of such deposits.

This application is a continuation-in-part of my co-pending applications, Serial Nos. 511,096 and 511,098, now Patent No. 2,843,509, both filed May 25, 1955, and 741,475, filed June 12, 1958.

One important present application of my invention is to power plants of modern aircraft, particularly jet engines, such as turbojet and turboprop power plants, which are constructed from special heat resistant alloys and super alloys. During service the various component parts are exposed to high operating temperatures in the vicinity of 800-1800° F. or even higher. At these elevated temperatures the metal alloys are exposed to both reducing and oxidizing atmospheres at various times and, as a result, very tightly adherent scale deposits are formed on the hot parts of the engine.

Examples of components of jet engines which are covered with scale deposits are the combustion chamber inner liner, cross-ignition tubes, transition liner, turbine nozzle assembly, and turbine rotor assembly (with attached buckets or turbine blades), and exhaust components.

The chief alloys used for jet engine components and on which the above-noted scales or deposits are formed include heat resistant stainless steels and heat resistant alloys, e.g., of the straight chrome type (martensitic or ferritic), austenitic stainless steels, stainless steels of the chromium or chromium-nickel type, and heat resistant alloys and super alloys including nickel base and cobalt base alloys, iron-chromium-nickel alloys, and cobalt-nickel-chromium alloys. These belong to the general classification of heat resistant alloys. The aforementioned deposits may also be formed on other types of alloys. These deposits, the heat scale or obdurate oxide deposits, are thus to be distinguished from ordinary rust produced by corrosion of mild steel and iron in their physical and chemical nature and are much more refractory and difficult to remove by alkaline reagents. For example, in the case of Inconel (a nickel base alloy) it appears most probable that the heat scale is largely a mixture of oxides with nickel oxide the major component. On stainless steels, the initial scale formed may be of the nature of an iron oxide-chromic oxide spinel. Also formed on the metal surfaces of aircraft engine parts during service are smut deposits. These hot scale deposits contain oxide layers of refractory nature and highly resistant to chemical and mechanical attack.

Also formed on the surface of the engine parts is a tough carbon or graphite scale which tightly adheres to the metal surfaces. In describing these scales as carbon or graphite scales I do not exclude the presence in the

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carbon deposits of high molecular weight asphaltene or asphaltic or tarry binders which are formed in the burning of the fuel. These deposits are found both intermingled with and deposited on the heat scale. In many cases massive carbon deposits are formed because of severe conditions of engine operation, especially in the case of "hot" spots. The heat scale formed on components of jet engines and other types of engines operating at high temperature under oxidizing conditions is a scale of oxide character known as "heat scale," which is deposited because of high temperature oxidizing conditions. Thus, at high temperatures of operation, e.g., existing in operation of jet engines, a heat scale is formed which is largely a mixture of the oxides of the metals or of the metal alloys of which the engine parts are constructed. The relative proportions of the various oxides of which such heat scale is composed may approach but need not correspond exactly with the percentages of the parent metals in the alloy.

For proper maintenance of the engines, overhaul procedures must be applied during which the engine components are completely and safely cleaned of heat scale deposits and any other contamination which may be present such as leaded deposits and deposits of carbon. One of the most important reasons for removing the foreign matter and scale deposits is to provide clean metal surfaces which are suitable for inspection for flaws by standard techniques. Inspection is especially important for jet engine parts which are highly stressed, such as nozzle guide vanes and turbine buckets.

Conventional procedures for cleaning jet engine hot section components during overhaul have been based on a combination of inadequate chemical cleaning methods plus mechanical cleaning, which includes grit blasting and liquid honing (or vapor blasting). Thus, for example, a conventional prior art procedure may include use of a chlorinated solvent, either hot or cold, followed by a caustic dip and then an alkaline permanganate treatment followed by a dip in dilute nitric acid, and finally vapor or sand blasting. However, these procedures have proved inadequate.

In oxidizing atmospheres obdurate, adherent oxide scale deposits are formed on the various alloys which require prolonged immersion times in a series of chemical baths to effectively remove the scale deposits, and provide clean parts for inspections.

While nitric acid has been employed as an after treatment of parts containing heat scale following treatment thereof in an alkaline, e.g., alkaline permanganate, bath, it has been observed in many instances that such nitric acid bath does not sufficiently loosen and remove the heat scale which has been previously conditioned in such alkaline bath.

One object of the invention is to remove heat scale deposits formed on engine components, particularly, but not exclusively, the "hot" sections of aircraft engines, especially jet engines.

Another object is to devise a procedure and compositions for the efficient removal of oxide deposits in the form of heat scale from parts carrying the same.

Still another object is to provide procedure and compositions for cleaning surfaces of metal components of engines, particularly aircraft engines, encrusted with oxide deposits or heat scale, to enable suitable inspection of the parts by production-line methods utilizing penetrant dyes or fluorescent materials.

A still further object of the invention is the provision

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of a method and compositions for accomplishing such descaling without producing any significant or detrimental amount of corrosion of the metal part during the cleaning or descaling cycle, so as to incur no significant weight loss or dimensional change of the metal or alloy of which the engine component is formed.

Yet another object is to devise procedure and compositions adapted to remove, particularly, heat scale deposits from engine parts, and at the same time achieving removal of carbon deposits if present.

A particular object is to afford a procedure and acid composition which is effective following an alkaline permanganate bath, for substantially completely dissolving and removing oxide or heat scale formed on engine parts at high temperatures, the oxide scale having been previously conditioned or oxidized to a higher valence state in an alkaline permanganate bath to condition the adhering heat scale to facilitate removability by the subsequent acid treatment in said acid composition.

A still further object is the provision of such an acid treating bath particularly suitable for completing removal of the heat scale, and employed in conjunction with and subsequent to treatment of parts containing heat scale first with an alkaline bath, particularly the alkaline bath containing complexing agent and alkanolamine of my aforementioned copending applications, followed by treatment in an alkaline permanganate bath, preferably the alkaline permanganate bath of my copending application Serial No. 741,475, filed June 12, 1958.

Other objects and advantages will appear from the description of my invention which follows:

I have found that heat scale deposits, which preferably have been previously conditioned by prior treatment in an alkaline bath or baths, can be readily loosened and substantially completely removed by treatment of the metal parts containing such conditioned heat scale in an aqueous nitric acid solution containing a complexing agent in the form of an aliphatic hydroxy carboxylic acid, which in conjunction with the nitric acid is effective in removal of the heat scale, is non-corrosive to the base metal of the parts being descaled, and is relatively stable in aqueous nitric acid at the elevated temperature of treatment, usually at least about 100° F.

The preferred aliphatic hydroxy acid is tartaric acid (dihydroxy succinic acid), but other such acids which may be employed include, for example, citric and malic acids, the effectiveness of tartaric and citric, however, being much superior to malic acid, as regards removal of heat scale in the nitric acid solution, according to the invention. The preferred tartaric acid may be employed in its asymmetric dextro or laevo forms, or the meso form or a dextro-laevo mixture. I ordinarily employ the commercially available form of tartaric acid which is composed essentially of the dextro rotatory type, and which I have found particularly effective. The term "tartaric acid" as employed in the specification and claims is intended to denote any of the above noted asymmetric forms or configurations of this acid or mixtures of two or more thereof.

In preferred practice of the invention, although not essential thereto, I also incorporate into the aqueous nitric acid, aliphatic hydroxy acid mixture a minor amount of a soluble complex fluoride which functions in conjunction with the aforementioned acids of the solution, to aid in complexing the heat scale components to facilitate decomposition thereof and form soluble compounds, and to thus aid in loosening and disintegrating the heat scale which preferably has been previously conditioned in the alkaline permanganate solution. An important requisite of such complex fluoride material is that it be of such nature and employed in such amounts as to be substantially non-corrosive to the base metal of the parts. Also, the complex fluoride should be relatively stable in the acid solution.

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The complex fluoride compounds employed in the invention are those forming a finite complex ion of fluorine and another element in solution. In such compounds fluorine is connected to the adjacent central atom by coordinate links, and said central atom has a coordination number of 4 to 7, as described in "Fluorine Chemistry," J. H. Simons, Academic Press, New York, 1950, pp. 21 to 25. This definition thus excludes hydrogen as a central atom and hence excludes the bifluorides. Illustrative examples of soluble complex fluorides which I can employ, their corresponding complex ions, and their coordination numbers are listed below.

	Complex Ion	Coordination Number
15		
Fluoberyllates.....	$\text{BeF}_4^-$	4
Fluoborates.....	$\text{BF}_4^-$	4
Fluoaluminates.....	$\text{AlF}_4^-$	4
20		
Fluoferrates.....	$\text{FeF}_6^{3-}$	6
Fluosilicates.....	$\text{SiF}_6^{2-}$	6
Fluotitanates.....	$\text{TiF}_6^{2-}$	6
Fluozirconates.....	$\text{ZrF}_6^{2-}$	6
Fluozirconates.....	$\text{ZrF}_7^{3-}$	7

25 Of these, I have found that the fluosilicates produce best results, with the fluotitanates next in line of preference. The fluoborates are not quite as effective as these aforementioned and require closer control to prevent corrosion. 30 These complex fluorides are used in the form of their soluble salts such as the alkali metal, e.g., sodium or potassium, or ammonium salts, or other soluble forms. A particularly useful and preferred complex fluoride is sodium silicofluoride, the potassium analog being of secondary preference.

35 While the incorporation of the above described complex fluorides in the aqueous nitric acid-aliphatic hydroxy acid solution is preferred to obtain enhanced descaling results, I can omit such fluorides and still obtain 40 improved results over the prior art aqueous nitric acid solutions used for this purpose, and not containing the aforementioned aliphatic hydroxy acid component.

I may also, if I desire, add other materials to the nitric acid solution of the invention. Thus, for example, 45 I may incorporate other acidic materials in the solution such as carboxylic acids, e.g., adipic acid.

The amount of nitric acid employed in my solution can be in the approximate range equivalent to from about 5 to about 30%, preferably about 10 to about 25%, by 50 volume of the solution of 42° Bé. nitric acid (67% by weight nitric acid). The amount of aliphatic hydroxy acid, preferably tartaric acid, employed generally ranges from about 2 to about 10, preferably about 4 to about 8, grams per 100 cc. of the aqueous diluted nitric acid 55 solution. The soluble complex fluoride, preferably silicofluoride, is employed in amounts in the approximate range of 0 to about 3, preferably from about .25 to about 1, and most desirably about .25 to about .5, grams per 100 cc. of the aqueous diluted nitric acid solution. 60 Where additional acids such as adipic acid are employed, the weight proportion of the hydroxy aliphatic acid, e.g., tartaric acid, to such additional acid, e.g., adipic acid, may range from about 50:1 to about 3:1. However, it is to be noted that the ranges and proportions given above 65 are not to be considered critical, but may be varied to some degree, with best results being realized by operating within such ranges and proportions.

The aqueous nitric acid solution of the invention can be prepared by first forming the dilute nitric acid solution and then adding the individual compound or compounds to the solution to form the desired treating composition according to the invention. However, a solid mixture of the compounds to be added to the dilute nitric acid can be prepared and packaged, and such mixture 70 added to the acid solution to form the desired solution. 75

Thus, for example, tartaric, citric or malic acid can be mixed with a source of soluble complex fluoride such as alkali metal silico-fluoride. If desired, other additives, e.g., adipic acid can also be included in the composition. The amount of ingredients present in such compositions can be about 50 to about 99 parts by weight of aliphatic hydroxy carboxylic acid, about 1 to about 50 parts by weight complex fluoride, preferably alkali metal, e.g., sodium, silicofluoride, and 0 to about 15 parts by weight adipic acid. The preferred ranges of such ingredients are about 75 to about 93 parts by weight of the aliphatic hydroxy acid, about 3 to about 15 parts complex fluoride and about 3 to about 12 parts adipic acid. Where adipic acid is not incorporated, the preferred amounts of the ingredients are about 80 to about 95 parts by weight of the aliphatic hydroxy acid and about 5 to about 15 parts complex fluoride. Ordinarily, about 6 to 16 ounces of this solid composition is dissolved in aqueous nitric acid per gallon of solution to form the solutions of the invention. However, it will be recognized that the amount so dissolved depends on the proportions of the ingredients in the particular composition involved.

It will be understood that the relative proportions of each of the ingredients of the compositions in the dry form and the concentration of the dry mixture used in the solution should be chosen so that when the dry mixture is added to the aqueous nitric acid solution, the amounts of the respective ingredients present in the solution will be preferably within the ranges specified above for the solution.

The aqueous nitric acid solution of the invention can be employed for descaling metal parts, e.g., engine parts, at a temperature ranging from about room temperature to as high as about 140° F. Preferably such solution is operated at elevated temperatures of at least about 100° F. in order to obtain substantially complete disintegration, loosening and removal of adherent heat scale. Where the nitric acid-aliphatic hydroxy acid solution does not contain any complex fluoride component, the operating temperature may be as high as about 140° F., i.e., a range of about 100 to 140° F. is utilized. Where, as in preferred operation the complex fluoride component described above is present in the bath, it is preferred not to operate at a temperature exceeding 120° F., i.e., operation is in the preferred range of about 100-120° F., in order to avoid any tendency of the complex fluoride to produce corrosion of the metal base of the part being descaled. The period of treatment in the aqueous nitric acid solution may range from about 5 minutes to about one hour, and is usually on the order of about 15 to about 30 minutes.

Where it is not desired to remove all of the heat scale from a part, the aqueous nitric acid solution of the invention can be employed alone in a single step to effectively remove a large portion of the heat scale. However, the instant aqueous nitric acid solution is particularly effective for removing adhering scale from metal parts, when such solution is employed subsequent to and in conjunction with a pretreatment in one or more solutions which function to condition and loosen the heat scale sufficiently so that it can be readily acted upon and dissolved by the nitric acid solution of the invention. These alkaline solutions also function to remove a portion of the heat scale. One such prior art type of pretreatment bath is an alkaline solution, e.g., fused caustic or potash or an aqueous alkaline permanganate solution. Where the heat scale is particularly heavy, fused sodium hydroxide or fused potassium hydroxide which may contain additives such as sodium nitrate or sodium hydride, can be employed for pretreatment. Usually, however, it is preferred to employ for pretreatment of the heat scale an alkaline permanganate solution which functions to oxidize to a higher state and to condition the heat scale for further loosening and disintegration thereof by my aqueous nitric acid bath.

Further, in preferred practice, especially where the heat scale is of a dense, obdurate type, as the first step in the process for removing heat scale prior to treatment in the alkaline permanganate bath, the metal or engine parts encrusted with heat scale are contacted with an alkaline solution, preferably of a type disclosed in my above copending application, Serial No. 511,096. These alkaline solutions contain a high concentration of alkali, a polyalkanol monoamine to which may be added an alkanol, preferably a polyalkanol, polyamine and the salt of a hydroxy aliphatic acid, or sometimes, depending on the function desired, a low molecular weight fatty acid. However, it is to be understood that the treatment of the parts in such solution prior to treatment in the alkaline permanganate solution is not always necessary, but is preferred.

However, when the engine parts encrusted with heat scale are pretreated in the aforementioned alkaline solution of my copending application, followed by further treatment and conditioning of the heat scale in alkaline permanganate solution, and then such parts are treated in the aqueous nitric acid solution of the invention for complete removal of loosened and conditioned heat scale, such heat scale is removed more rapidly and much more completely, or a significantly greater percentage of heat scale is removed for a given time, than when employing the same procedure but using a conventional aqueous nitric acid solution not containing aliphatic hydroxy acid, e.g., tartaric acid.

In the highly alkaline solutions preferably employed as the first step in the process and disclosed in application, Serial No. 511,096, the amount of alkaline material employed may range to give in solution free alkali metal hydroxide equivalent to from about 4% to about 40% by weight alkali metal oxide (e.g.,  $K_2O$ ,  $Na_2O$ ) based on the weight of the solution. Preferably, from about 10-25% of alkali, most desirably potassium hydroxide, is used to obtain the desired high alkalinity.

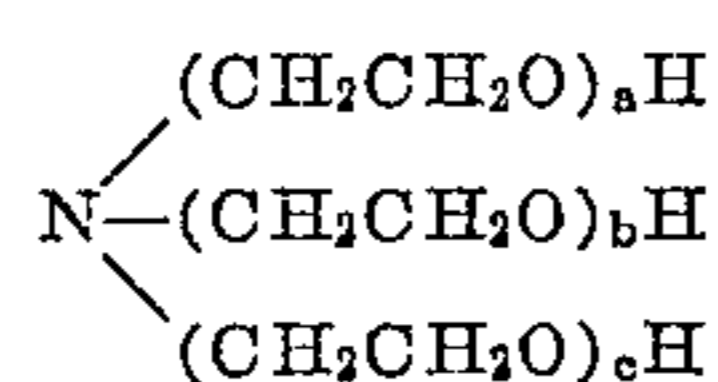
In these solutions there also are incorporated compounds in the form of certain complexing salts, to act in conjunction with the alkali. These salts are derived from an aliphatic hydroxy acid such as lactic, citric, tartaric, gluconic, glyceric, malic, glycollic acid, and saccharic acid. These salts or mixtures of these salts may be employed for the above purpose. Low molecular weight fatty acid such as acetic or propionic acid may also be employed. These latter salts, however, are not as useful in such solutions as are the salts of the hydroxy acids referred to above. They may be used effectively particularly if used together with the hydroxy acids. The soluble salts of the above acids are employed, preferably employing the potassium or sodium salt, for example, potassium or sodium acetate or potassium or sodium glycollate. The quantity of these complexing salts added to the solution may vary, but generally from about 1 to about 45% by weight of such salts can be present in the treating solution in water, amounts of about 4 to about 40% usually being employed. These salts can be used separately or in admixture with each other, and function to a degree in complexing heat scale components, e.g. oxides of the base metal, to facilitate removal thereof, and also function to complex with any leaded deposits which may be present, e.g. in the form of lead salts such as oxides, to produce soluble compounds.

Also, alkanolamines are employed in the above alkaline solutions containing the salts of the aliphatic hydroxy acids or low molecular weight fatty acids. As alkanolamines the polyalkanolamines are preferably employed, particularly those which form stable dispersions or solutions in the water system of the composition at the operating temperatures of 200 to 300° F. and are not decomposed by pyrolysis at such temperatures under the conditions of proposed use. Examples of suitable polyalkanolmonoamines with their boiling points and vapor pressures (at 20° C.) of the pure compounds are set out below.

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TABLE I

Name	Boiling Pt. at 760 mm. pressure		Vapor Pressure, mm. Hg at 20° C.
	° C.	° F.	
Diethanolamine.....	250	480	less than 0.01
Triethanolamine.....	360	680	Do.
N-aminoethyl ethanolamine.....	244	471	Do.
N-methyl diethanolamine.....	247	476	Do.
N-ethyl diethanolamine.....	252	485	Do.
Diisopropanolamine.....	259	480	Do.
Triisopropanolamine.....	306	583	Do.

Other suitable polyalkanolmonoamines are hydroxypropyl diethanolamine, hydroxyethyl diisopropanolamine, N,N-dihydroxyethyl glycine, and glycol or polyglycol derivatives of triethanolamine and polyetherglycol derivatives of triethanolamine having the general constitutional formula



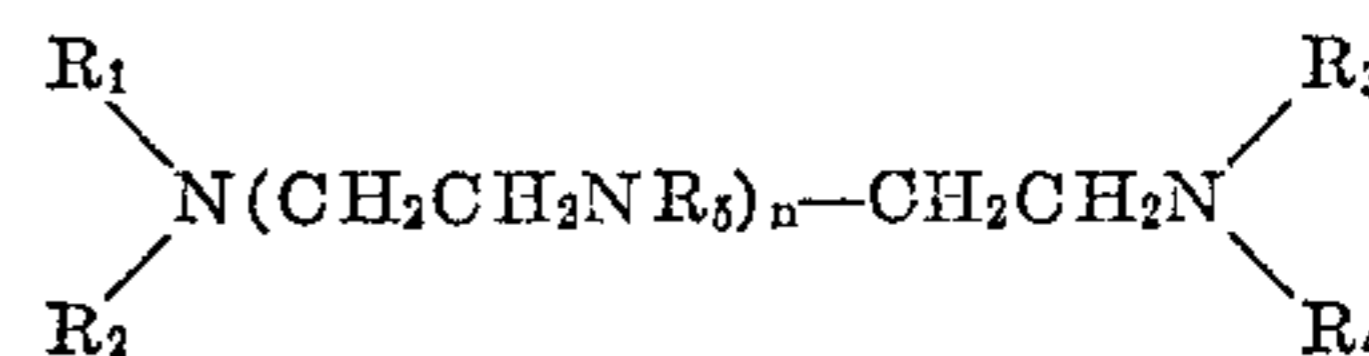
where  $a+b+c$  equals from 3-6, both inclusive. Triethanolamine or homologues thereof wherein one or two of the hydroxyethyl groups are replaced by hydroxypropyl groups should be present either alone or together with one or more other suitable monoamines or polyamines described below.

I may also use alkanolpolyamines, preferably polyalkanolpolyamines, having boiling points above 400° F. and similar low vapor pressures such as the polyalkanolpolyamines referred to below. Alkanolpolyamines may be used to partially replace the alkanolmonoamines in

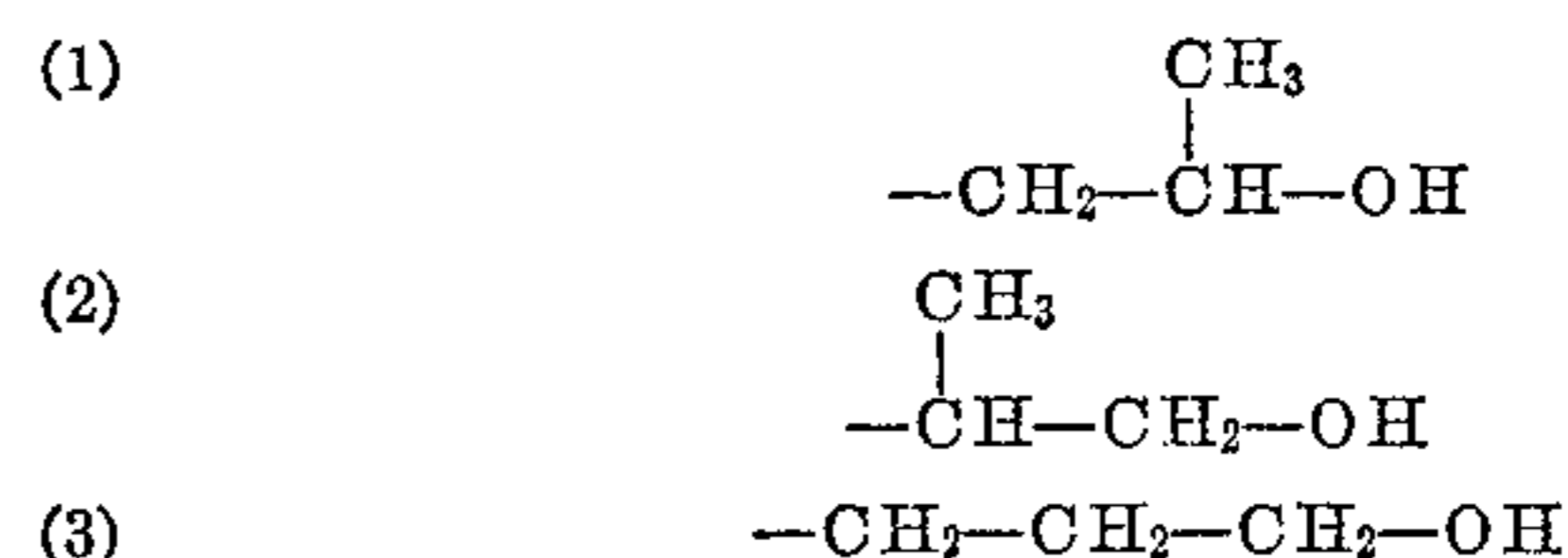
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a substantial proportion of the heat scale is in most instances removed. The result is an improvement in overall cleaning ability and performance particularly in the rate of removal of the heat scale and also carbon.

5 Examples of suitable alkanolpolyamines for purposes of the invention have the following general formula:



10 where  $n$  equals 0 to 4, preferably 0 to 1.  $\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4$  and  $\text{R}_5$  may be hydrogen, hydroxyethyl, hydroxypropyl, or carboxymethyl groups. Where  $n$  equals 0 there is at least one hydroxyethyl group present, and where there is only one hydroxyethyl group there is also present at least one carboxymethyl group, and preferably two or three carboxymethyl groups. Where  $n$  is 1 or more, there are a plurality of hydroxyalkyl groups present, e.g. 2 or more. All of these groups may be hydroxyethyl groups or hydroxypropyl groups, or a portion of these hydroxyalkyl groups may be hydroxyethyl and the remainder hydroxypropyl. Where there are two hydroxyalkyl groups present, there may also be present one or more carboxymethyl groups. The hydroxypropyl structure can be any of the following structures:



Structure (1) is the grouping preferably employed.

35 Examples of suitable specific alkanolpolyamines where  $n=0$  are tabulated below:

TABLE Ia

	$\text{R}_1$	$\text{R}_2$	$\text{R}_3$	$\text{R}_4$
(1)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$	H	H
(2)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$	H
(3)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$
(4)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	H	H
(5)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>	H	H
(6)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$	H
(7)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$
(8)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	H	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>	H
(9)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	H
(10)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$
(11)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	H
(12)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2\text{CO}-\text{OH}$
(13)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$
(14)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>
(15)---	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>
(16)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>
(17)---	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>	$-\text{CH}_2-\text{CH}-\text{OH}$   CH <sub>3</sub>

like weight proportions or the alkanolpolyamines may be employed in additional weight proportions to the polyalkanolmonoamines in the manner described hereinbelow to assist and improve the removal of carbonaceous deposits and heat scale.

In preferred practice another alkanolamine, preferably an alkanolpolyamine, is also incorporated with the polyalkanolmonoamine. When using the alkanolpolyamines,

The alkanolpolyamines listed in Table Ia have boiling points above 400° F.

70 Of the above compounds in Table Ia the tetra-kia N-hydroxyethyl ethylenediamine (Compound 13), the tetra-kis N-hydroxypropyl ethylenediamine (Compound 15), N-monohydroxyethyl, N-trihydroxypropyl ethylene diamine (Compound 16), and N-dihydroxyethyl, N-dihydroxypropyl ethylene diamine (Compound 17) are of par-

ticular importance. Examples of polyalkanolpolyamines where  $n$  is 1 or more are pentahydroxyethyl diethylene triamine, hexahydroxyethyl triethylene tetramine and heptahydroxyethyl tetraethyl pentamine.

Preferably these alkanolpolyamines should not be so extensively substituted as to disadvantageously impair their solubility and stability in the alkaline solution or to disadvantageously alter their characteristics as an alkanolpolyamine.

The amount of alkanolamine employed, which may be polyalkanolmonoamine alone, or which may include both polyalkanolmonoamine in combination with alkanolpolyamine, is generally in the range of about 2.5 to about 30%, preferably about 10 to about 30%, by weight of the solution. Where, as in preferred practice, the alkanolmonoamines are employed in admixture with alkanolpolyamines, the range of ratios of the amounts of monoamine to polyamine by weight can be between about 1 part monoamine to 1 part polyamine, to about 50 parts monoamine to 1 part polyamine, but preferably this range of ratios is between about 1:1 to about 10:1.

Phenols in the form of alkali metal phenates such as the potassium and sodium phenates may also be added, if desired, to the above alkaline solution containing complexing salt and alkanolamine. Thus, the phenols, i.e., the monatomic phenols are suitable such as hydroxybenzene and its homologues including cresol and cresylic acid, polyatomic phenols such as the dihydroxy benzenes and its homologues, triatomic phenols such as pyrogallol and its homologues, and higher polyphenols, which are sufficiently acid to form salts with alkali at the concentrations employed which are soluble in these aqueous compositions at the temperature of the treatment, to wit, at 200–300° F. The alkali metal salts which are effective in this respect are the salts of phenol itself, the ortho, meta and para dihydroxy benzenes, and of the trihydroxy benzenes such as pyrogallic acid. These materials are generally compatible with the alkali solutions. Hence, such materials can be employed as additive to the treating reagent. Such phenates may be employed in amounts ranging up to about 20% by weight of the alkaline solution, generally about 3 to 15%.

The above alkali solution containing a salt of a hydroxy aliphatic acid or the salt of a low molecular weight fatty acid and alkanolamine is effective for both carbon and heat scale removal.

A typical alkaline solution of this type can be produced by adding the ingredients listed below to water in the amount noted below.

Solution A:	Wt. percent of solution
Potassium hydroxide.....	38
Triethanolamine .....	13.7
Tetra - kis N - (2 - hydroxypropyl) ethylenedi- amine .....	2.6
Acetic acid.....	3.8
Hydroxy acetic acid (70% water solution)....	21.0
Phenol .....	4.7
Potassium acid tartrate.....	0.2
Water .....	16.6

The parts may then be treated in a second step of the process in an alkaline permanganate solution which removes a portion of the heat scale and oxidizes the remaining heat scale to a condition rendering it readily loosened and removed in my aqueous nitric acid bath. This alkaline permanganate treatment is particularly employed where the heat scale is tightly adherent and refractory, and especially if glazed over. Such permanganate solution contains an alkali metal hydroxide, e.g. sodium or potassium hydroxide and a soluble permanganate, preferably alkali metal, e.g. potassium or sodium permanganate as oxidizing agent. This composition may also contain an alkali metal carbonate. The amount of alkali metal hydroxide employed may range from about 1 to about 25% by weight of solution, preferably about

10 to about 25%, the amount of permanganate from about 0.4 to about 12% by weight of solution, preferably about 3 to about 9%, and the amount of alkali metal carbonate from 0 to about 15%, usually about 5 to 15%.

A typical solution of this type is as follows:

Solution B	Solution	
	oz/gal.	percent by Weight
Sodium hydroxide.....	18	9.8
Sodium carbonate.....	18	9.8
Potassium permanganate.....	8.5	4.6
Water.....	1 gal	75.8

A preferred type of alkaline permanganate solution is one which contains a water soluble inorganic fluoride derived from any source which produces fluoride containing ion in strong alkaline solution, as described in my copending application, Serial No. 741,475, filed June 12, 1958. The fluoride may be a simple fluoride such as the alkali metal fluorides sodium or potassium fluoride, or ammonium fluoride, or I can employ complex fluorides such as fluoborates and silicofluorides, e.g. sodium, potassium, or ammonium fluoborates or silicofluorides. These complex fluorides decompose in the alkaline-permanganate system to produce the fluoride ion in the solution. The amount of fluoride which I employ is generally in the range of about 1 to about 8% by weight of the solution, usually about 2 to 6%. However, for any specific fluoride ion source employed, it is preferred not to employ an amount substantially greater than the amount which is soluble in the particular alkaline permanganate solution utilized.

A typical solution of this type is as follows:

Solution D	Solution	
	oz/gal.	Percent by weight of solution
Potassium hydroxide.....	43.2	22.8
Potassium permanganate.....	12.0	6.2
Sodium fluoride.....	5.6	2.3
Water.....	Balance	Balance

The parts are immersed in the alkaline permanganate solution, preferably containing fluoride, maintained at a temperature generally in the range of about 180 to about 220° F., preferably 190 to 210° F. Time of treatment is from say about 15 minutes to about 1½ hours where pretreatment with the highly alkaline solutions of my copending application, Serial No. 511,096, takes place prior to use of the permanganate bath. Longer periods may be required where the alkaline permanganate solution is used without prior treatment in the alkaline solutions containing alkanolamine of Serial No. 511,096. The parts are then removed, rinsed by dip or spray with water and then treated in the aqueous nitric acid solution herein described to remove the heat scale loosened and conditioned in the alkaline permanganate bath. Following treatment in the aqueous nitric acid bath of the invention described above, the parts are then rinsed free of adhering acid solution.

Treatment in the aqueous nitric acid solution of the invention can also be employed as a first step in the procedure for removal of heat scale, followed by treatment in the aforementioned alkaline solutions, and also, if desired, treatment in the aqueous nitric acid solution hereof can also be an intermediate step between alkaline treating steps, to aid in loosening and conditioning the heat scale for eventual removal thereof. Hence, the aqueous nitric acid solution hereof can be employed in one or more steps of a process for removal of heat scale in combination with one or more alkaline treating steps.

As illustrations but not as limitations of the invention, the following are given by way of examples:

#### Example 1

Turbine buckets of Stellite 31 alloy (a cobalt base alloy) from a PRT (Power Recovery Turbine) and jet engine combustion chamber inner liners made of Inconel (a nickel base alloy), all coated with heat scale, were first treated in the above solution A for 30 minutes at 275° F., then in solution B maintained at about 210° F. for 30 minutes, and then in the following aqueous solution E for 30 minutes at 100° F.

Solution E:	Proportions
20% by vol. in water of 42° Baumé nitric acid	cc. 100
Tartaric acid	grams 5
Sodium silicofluoride, Na <sub>2</sub> SiF <sub>6</sub>	do 0.5

A 97 to 98% descaling or removal of the heat scale from these parts was observed with substantially no corrosion of the base metal of the turbine buckets taking place.

#### Example 2

A similar procedure to that of Example 1 was followed except that 10% by volume in water of 42° Baumé nitric acid was used in solution E. About 95% descaling was observed on the parts.

#### Example 3

Similar turbojet engine turbine buckets, of Stellite 21 alloy (a cobalt base alloy), covered with heat scale, carbon and lead oxide deposits from combustion of leaded fuel, were treated as follows:

The parts were treated in a solution for 30 minutes at 210° F., said solution being formed by adding composition F to water in a proportion of 2 lbs. per gallon of water.

Composition F:	Weight percent
Sodium hydroxide	80
Sodium acetate	6
Potassium acid tartrate	12
Santomerse (marketed by Monsanto Chemical Co.—an alkyl benzene sulfonate having 7 to 8 carbon atoms in the molecule)	2

This treatment substantially removed loose carbon and most of the leaded deposits (including lead oxide and other lead salts).

The parts were then treated in solution A above for 30 minutes at 270° F., removing residual leaded deposits, a substantial amount of the heat scale and also removing carbon deposits.

The parts were then treated in solution D above for 30 minutes at 210° F., removing a substantial portion of the remaining heat scale.

The parts were then rinsed in the usual manner after each of the above treatments.

The parts so treated were then separated into 5 portions and the respective portions subsequently treated for 30 minutes in the respective solutions G, H, J, K and L given in Table II below, each solution maintained at 100° F. The percentage of heat scale removal or the amount of descaling which took place in each solution is also noted below. In solutions G to K, the proportions of tartaric acid and Na<sub>2</sub>SiF<sub>6</sub> are based on 100 cc. of the diluted 42° Bé. nitric acid solution.

TABLE II

Solution	Percent by volume in H <sub>2</sub> O of 42° Bé. HNO <sub>3</sub>	Tartaric Acid (grams)	Sodium Silico fluoride (grams)	Percent Descaled
G	20	—	—	80
H	20	5	—	94
J	20	7.5	—	95
K	20	5	0.25	97
L	20	5	0.5	99

To illustrate one way of producing solutions, in the case of solution K, this solution is produced by first forming the dilute nitric acid solution and adding thereto about 6.5 ounces per gallon of a solid mixture composed of about 95.2 parts by weight tartaric acid and about 4.8 parts by weight sodium silicofluoride. Solution L can be formed in a similar manner, except that the amount of Na<sub>2</sub>SiF<sub>6</sub> in the mixture is doubled.

As shown in Table II, all of the aqueous nitric acid solutions H to L of the invention, containing tartaric acid, were much more effective (producing 94 to 99% removal of heat scale) as contrasted to the prior art dilute nitric acid solution G not containing tartaric acid (producing only 80% heat scale removal). Further, it is seen that when the amount of tartaric acid in solution H was increased to 7.5 grams per 100 cc. dilute nitric acid solution in solution K, an improvement in result was observed; when Na<sub>2</sub>SiF<sub>6</sub> was added as in solutions K and L, a still further improvement was realized; and the latter improvement was further enhanced when the amount of Na<sub>2</sub>SiF<sub>6</sub> was increased to 0.5 gram per 100 cc. of dilute nitric acid solution, as shown by the results for solution L, wherein 99% descaling was obtained.

#### Example 4

Turbine buckets of Stellite 21 alloy, covered with leaded deposits, carbon and heat scale of a dense and tenacious nature, were processed through solutions F, A and D in the same manner and under the same conditions as set forth in Example 3.

The parts so treated were then separated in separate portions and each portion subsequently respectively treated for 30 minutes in the respective solutions M to U indicated in Table III below, each maintained at 100° F. The proportions of tartaric acid and sodium silicofluoride set forth in each composition are on the basis of 100 cc. of the dilute 42° Bé. nitric acid solution employed therein.

TABLE III

Solution	Percent by volume in H <sub>2</sub> O of 42° Bé. HNO <sub>3</sub>	Tartaric acid (grams)	Sodium Silico fluoride (grams)	Percent Descaled
M	10	—	—	65
N	20	—	—	65
O	10	5	—	80
P	15	5	—	90
Q	20	5	—	90
R	10	5	0.5	95
S	20	5	0.5	95
T	—	5	—	50
U	—	5	0.5	50

From Table III above, it is seen that nitric acid alone results in only 65% removal of heat scale, and an aqueous solution of tartaric acid alone, or an aqueous solution of tartaric acid and sodium silicofluoride, results in only 50% descaling. On the other hand, the addition of tartaric acid to aqueous nitric acid according to the invention results in improved descaling of the order of 90% when the nitric acid concentration is increased to 15 to 20% by volume of 42° Bé. nitric acid. Further, an additional improvement to about 95% descaling is realized by addition of sodium silicofluoride to the nitric-tartaric acid solution. The results of Table III clearly show the synergistic effect of the nitric-tartaric acid combination, or of the nitric-tartaric acid-silicofluoride combination of the invention in obtaining markedly improved results, particularly over the prior art use of aqueous nitric acid.

#### Example 5

Similar turbine buckets of S-816, a chromium-nickel-cobalt alloy, covered with heat scale, carbon and leaded deposits (lead oxide and other lead salts) were processed as follows:

Step 1.—The parts were treated in an aqueous solution at 210° F. for 30 minutes, of composition F above,

formed by adding composition F to water in a proportion of 2 lbs. of composition F per gallon of water, removing leaded deposits.

Step 2.—The parts were then treated in solution V below at 275° F. for 30 minutes, removing carbon deposits and a substantial portion of the heat scale.

Solution V:	Percent by weight	
Potassium hydroxide.....	36.1	
Triethanolamine .....	12.3	10
Acetic acid.....	11.7	
Potassium acid tartrate.....	1.9	
Tetrahydroxyethyl ethylene diamine.....	4.5	
Monohydroxyethyl trihydroxypropyl ethylene diamine .....	6.7	15
Water .....	26.8	
	100.0	

Step 3.—The parts were then treated in solution D at 210° F. for 30 minutes, removing additional heat scale and loosening and conditioning the remaining heat scale for treatment thereof in the subsequent nitric acid solution.

Step 4.—A portion of the parts so treated in steps 1 to 3 above were then treated in 25% by volume in water of 42° Bé. nitric acid, designated solution W, at 100° F. for 30 minutes, and the remaining parts previously treated in steps 1, 2 and 3 above, were then treated in a solution X, at 100° F. for 30 minutes, said solution X being formed by adding the solid composition X' below to a dilute nitric acid solution of 25% by volume in water of 42° Bé. nitric acid, in a proportion of 12 ounces of said composition per gallon of water.

Composition X':	Parts by weight	
Tartaric acid.....	80	35
Adipic acid.....	15	
Sodium silicofluoride.....	5	

Solution X contains, per 100 cc. of the diluted nitric acid, about 7.44 grams tartaric acid, about 1.4 grams adipic acid and about 0.47 gram sodium silicofluoride.

The parts treated in solution W in the fourth step showed 88% removal of heat scale, and the other parts treated in solution X showed 98% removal of heat scale, a substantial improvement over the prior art nitric acid solution W under the above conditions of treatment.

#### Example 6

Similar J-34 engine turbine buckets of Stellite 21 alloy covered with heat scale, carbon and leaded deposits were processed as follows:

The parts were first treated in steps 1, 2 and 3 of Example 5, by means of the same procedure and solutions as in these respective steps of Example 5, except that treatment in steps 2 and 3 was for 45 minutes in each of these steps. Such treatment removed carbon and leaded deposits and a substantial portion of the heat scale.

The parts were then separated into 5 portions, the first portion being treated in solution W (see Example 5) for 30 minutes at 100° F., the second portion treated in solution X (see Example 5) for 30 minutes at 100° F., and the third portion treated in solution X for 15 minutes. The fourth portion was treated in solution Y at 100° F. for 30 minutes, solution Y being formed by adding the solid composition Y' given below to 25% by volume in water of 42° Bé. nitric acid, in a proportion of 9 ounces of said composition per gallon of solution.

Composition Y':	Parts by weight	
Tartaric acid.....	89.2	70
Adipic acid.....	3.4	
Sodium silicofluoride.....	7.4	

Solution Y contains, per 100 cc. of the diluted nitric acid, about 6.24 grams tartaric acid, about 0.24 gram adipic acid, and about 0.52 gram sodium silicofluoride.

The fifth portion of the parts previously treated in steps 1, 2 and 3 above, were treated in solution Y for 15 minutes at 100° F.

The descaling results are given in Table IV below.

TABLE IV

	Percent removal of heat scale
(a) Parts treated in solution W.....	50
(b) Parts treated in solution X for 30 minutes...	99-100
(c) Parts treated in solution X for 15 minutes...	96
(d) Parts treated in solution Y for 30 minutes...	99
(e) Parts treated in solution Y for 15 minutes...	94

From Table IV above it is seen that treatment of the parts in solutions X and Y of the invention containing the ingredients tartaric acid and sodium silicofluoride resulted in markedly improved descaling of 94% or better, as contrasted to 50% descaling of the parts treated in the prior art nitric acid solution W not containing said ingredients. It is also noted that an increase in the period of treatment from 15 to 30 minutes in solutions X and Y produced practically complete (that is, 99 to 100%) removal of heat scale.

#### Example 7

Stellite 21 alloy turbine buckets coated with heat scale, carbon and leaded deposits were treated by the procedure and solution of step 1 of Example 5, thus removing leaded deposits. The parts were then treated in solution A at 275° F. for 60 minutes, removing carbon deposits and a substantial portion of heat scale, and the parts were then treated in solution D at 210° F. for 30 minutes, loosening and conditioning the remainder of the heat scale. The parts were finally treated in a solution at 100° F. for 30 minutes, containing 20% by volume in water of 42° Bé. nitric acid and citric acid in a proportion of 5 grams citric acid per 100 cc. of the diluted nitric acid. The parts so treated had 98.5% of the heat scale removed.

#### Example 8

A similar procedure to that of Example 1 can be carried out on parts similar to those disclosed therein, but replacing the sodium silicofluoride with sodium fluoritanate. Improved descaling results are obtainable similar to the results of Example 1.

#### Example 9

A similar procedure to that of Example 7 can be carried out on parts similar to those disclosed therein, but replacing the citric acid with the same amount of malic acid. The descaling results thereby obtainable are of the order of about 90% heat scale removal.

#### Example 10

Turbine buckets of Stellite 21 alloy and having heat scale deposits were heated for 30 minutes with fused potassium hydroxide at 750° F. The parts were then treated in permanganate solution B above, and then treated in a 25% by volume 42° Bé. nitric acid solution for 30 minutes. Following rinsing, it was observed that about 90% removal of heat scale was obtained.

The above procedure was repeated, but incorporating tartaric acid in the nitric acid solution in an amount of 6.5 grams tartaric acid per 100 cc. of the nitric acid solution. About 98% removal of heat scale was indicated here, demonstrating the effectiveness of the nitric acid-tartaric acid solution when used in conjunction with a prior art caustic pretreatment step.

The nitric acid solutions of the invention have practically no corrosive effect on the base metal of the parts treated to remove heat scale. Thus, for example, the penetration of such solution into the metal is only on the order of about  $7 \times 10^{-6}$  inch or less for one hour treatment at 100° F.

It is to be understood that the descaling results obtained in the foregoing examples bear no relation to the results given in the treatments described in my copending application Serial No. 511,096, and particularly Table V thereof, since comparisons are only valid when made on substantially identical parts having substantially identical heat scale deposits, such parts resulting from simultaneous operation in engines with identical thermal histories, identical alloys and identical surface conditions prior to thermal operations. The parts tested in the instant application were not identical in these respects with the parts used in my copending application Serial No. 511,096, particularly in connection with the tests, results of which are reported in Table V thereof.

From the foregoing it is seen that the process and aqueous nitric acid compositions hereof have as a particular advantage, providing loosening and substantially complete removal of heat scale following prior conditioning of the heat scale in alkaline solutions. As a result of my novel compositions and process, a greater proportion of the heat scale can be removed than is ordinarily the case with conventional nitric acid solutions for the same time period, or the same amount of heat scale can be removed according to the invention for a shorter time period of treatment than when employing conventional nitric acid solutions. My process and compositions are particularly valuable for removing the last 10 to 20% of the heat scale on engine parts, which is usually the most difficult portion to remove.

The term "consisting essentially of" as used in the definition of the ingredients presents in the compositions claimed is intended to exclude the presence of other materials in such amounts as to interfere substantially with the properties and characteristics possessed by the composition set forth but to permit the presence of other materials in such amounts as not substantially to affect said properties and characteristics adversely.

While I have described particular embodiments of my invention for purposes of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention as set forth in the appended claims.

I claim:

1. In the process of removal of heat scale on a metal object, the step of treating said object in an aqueous solution consisting essentially of nitric acid and an aliphatic hydroxy carboxylic acid of the group consisting of tartaric, citric and malic acids.

2. In the process of removal of heat scale on a metal object, the step of treating said object in an aqueous solution consisting essentially of nitric acid and an aliphatic hydroxy carboxylic acid of the group consisting of tartaric, citric and malic acids, said nitric acid being present in a concentration equivalent to from about 5 to about 30% by volume of the aqueous solution, of 42° Bé. nitric acid, and said aliphatic acid being present in a proportion of about 2 to about 10 grams per 100 cc. of the aqueous nitric acid solution.

3. In the process of removal of heat scale on a metal object, the step in claim 1, wherein said aliphatic acid is tartaric acid.

4. In the process of removal of heat scale on a metal object, the step of claim 1, wherein said aliphatic acid is citric acid.

5. In the process of removal of heat scale on a metal object, the step of claim 1, wherein said aliphatic acid is tartaric acid, said nitric acid being present in a concentration equivalent to from about 10 to about 25% by volume of the aqueous solution, of 42° Bé. nitric acid, said tartaric acid being present in a proportion of about 4 to about 8 grams per 100 cc. of the aqueous nitric acid solution.

6. In the process of removal of heat scale on a metal object, the step of treating said object in an aqueous nitric acid solution containing tartaric acid and a soluble

complex fluoride forming in solution a complex ion of fluorine and an atom of an element having a coordination number of 4 to 7, the fluorine atom in said complex being coordinately linked to said atom.

7. The process for removal of heat scale on metal parts which comprises treating said heat scale in an alkaline bath and then treating said heat scale in an aqueous nitric acid solution containing an aliphatic hydroxy carboxylic acid of the group consisting of tartaric, citric and malic acids.

8. The process for removal of heat scale on metal parts by conditioning said heat scale in an alkaline bath followed by treating the conditioned heat scale in an aqueous nitric acid solution containing tartaric acid.

9. The process for removal of heat scale on metal parts which comprises treating said heat scale in an alkaline bath to condition said heat scale and treating the conditioned heat scale in an aqueous nitric acid solution containing tartaric acid and a complex fluoride of the group consisting of the soluble fluoberyllates, fluoferrates, fluosilicates, fluoborates, fluotitanates, fluoaluminates and fluozirconates, to remove said heat scale.

10. The process for removal of heat scale on metal parts which comprises treating said heat scale in an alkaline bath to condition said heat scale, and treating the conditioned heat scale in an aqueous nitric acid solution containing tartaric acid and alkali metal silicofluoride, to remove said heat scale.

11. The process for removal of heat scale on metal parts which comprises treating said heat scale in an alkaline bath to condition said heat scale, and treating the conditioned heat scale in an aqueous nitric acid solution containing tartaric acid, adipic acid and alkali metal silicofluoride, to remove said heat scale.

12. The process for removal of heat scale on metal parts which comprises treating said heat scale in an alkaline bath to condition said heat scale, and treating the conditioned heat scale in an aqueous solution consisting essentially of nitric acid in a concentration equivalent to about 5 to about 30% by volume of said solution of 42° Bé. nitric acid, about 2 to about 10 grams of tartaric acid per 100 cc. of said solution, 0 to about 3 grams of alkali metal silicofluoride per 100 cc. of said solution, and adipic acid in an amount such that the weight proportion of said tartaric acid to said adipic acid is from about 50:1 to about 3:1.

13. The process for removal of heat scale from an engine part which comprises contacting said part with a water solution containing from about 10 to 25% by weight of an alkali metal hydroxide, from about 1 to about 45% by weight of an agent taken from the group consisting of soluble salts of the aliphatic hydroxy acids and soluble salts of the low molecular weight fatty acids, and from about 2.5 to about 30% by weight of an alkanolamine, then contacting said parts with a water solution containing from about 10 to 25% by weight of an alkali metal hydroxide, from about 0.4 to 12% of an alkali metal permanganate, and from about 1 to 8% of a soluble inorganic fluoride which produces the fluoride containing ion in said alkaline solution, and then contacting said part with an aqueous solution consisting essentially of nitric acid in a concentration equivalent to about 5 to about 30% by volume of said solution of 42° Bé. nitric acid, about 2 to about 10 grams of tartaric acid per 100 cc. of said solution, 0 to about 3 grams of alkali metal silicofluoride per 100 cc. of said solution and adipic acid in an amount such that the weight proportion of said tartaric acid to said adipic acid is from about 50:1 to about 3:1.

14. An aqueous acid solution for removal of heat scale from metal parts which consists essentially of nitric acid, an aliphatic hydroxy carboxylic acid of the group consisting of tartaric, citric and malic acids, and a soluble complex fluoride forming in solution a complex ion of fluorine and an atom of an element having a coordination number



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of 4 to 7, the fluorine atom in said complex being coordinately linked to said atom.

15. An aqueous acid solution for removal of heat scale from metal parts which consists essentially of nitric acid, tartaric acid and a complex fluoride of the group consisting of the soluble fluoberyllates, fluoferrates, fluosilicates, fluoborates, fluotitanates, fluoaluminates and fluozirconates.

16. An aqueous acid solution for removal of heat scale from metal parts which consists essentially of nitric acid in a concentration of from about 5 to about 30% by volume of the aqueous solution, of 42° Bé. nitric acid, about 2 to about 10 grams of tartaric acid per 100 cc. of said solution, and 0 to about 3 grams of alkali metal silicofluoride per 100 cc. of said solution.

17. An aqueous acid solution for removal of heat scale from metal parts which consists essentially of nitric acid in a concentration equivalent to from about 10 to about 25% by volume of the aqueous solution, of 42° Bé. nitric acid, about 4 to about 8 grams of tartaric acid per 100 cc. of said solution, and about .25 to about 1 gram of sodium silicofluoride per 100 cc. of said solution.

18. An aqueous acid solution as defined in claim 7, including adipic acid in an amount such that the weight proportion of said tartaric acid to said adipic acid is from about 50:1 to about 3:1.

19. A composition of matter which when added to an aqueous nitric acid solution forms a solution suitable for removal of heat scale from metal parts composed of heat resistant alloys, which consists essentially of about 50 to about 99 parts by weight of an aliphatic hydroxy carboxylic acid of the group consisting of tartaric, citric and malic acids, and about 1 to about 50 parts by weight of a soluble complex fluoride forming in solution a complex ion of fluorine and an atom of an element having a coordination number of 4 to 7, the fluorine atom in said complex being coordinately linked to said atom, said components of the composition forming the major proportion thereof.

20. A composition as defined in claim 19, wherein said complex fluoride is a member of the group consisting of the soluble fluoberyllates, fluoferrates, fluosilicates, fluoborates, fluotitanates, fluoaluminates and fluozirconates.

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21. A composition of matter which when added to an aqueous nitric acid solution forms a solution suitable for removal of heat scale from metal parts composed of heat resistant alloys, which consists essentially of about 50 to about 99 parts by weight of tartaric acid and about 1 to about 50 parts by weight of an alkali metal silicofluoride, said components of the composition forming the major proportion thereof.

22. A composition of matter which when added to an aqueous nitric acid solution forms a solution suitable for removal of heat scale from metal parts composed of heat resistant alloys, which consists essentially of about 75 to about 93 parts by weight of tartaric acid, about 3 to about 15 parts by weight sodium silicofluoride and about 3 to about 12 parts by weight of adipic acid, said components of the composition forming the major proportion thereof.

23. A composition of matter which when added to an aqueous nitric acid solution forms a solution suitable for removal of heat scale from metal parts composed of heat resistant alloys, which consists essentially of about 80 to about 95 parts by weight of tartaric acid and about 5 to about 15 parts by weight of sodium silicofluoride, said components of the composition forming the major proportion thereof.

24. A composition of matter as defined in claim 19, including adipic acid in an amount up to about 15 parts by weight of said composition.

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