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COMPOSITION FOR RADIOACTIVE DECONTAMINATION AND DESCALING OF COBALT ALLOYS
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This invention relates to a novel composition and process for the radioactive decontamination of surfaces on which are deposited radioactive materials, and for removal of scale or deposits from the surface of metal parts.

In my copending application, Serial No. 804,573, filed on even date herewith, I have described a process for effectively removing radioactive contaminants from metal surfaces, particularly from the internal surface of the components of nuclear reactors or nuclear power generating equipment, including the water circulation loop piping and associated equipment. By the process described in said copending application such radioactive contaminants can be removed practically completely. Where scale deposits are present, which may include both tight and loosely adherent scale, generally of an oxide character, and in which deposits the radioactive contaminants are contained, the scale can be removed together with the radioactive contaminants or emitters. Thus, said process is effective for removing radioactive contamination and scale deposits simultaneously where both are present.

The process of my said copending application in preferred practice briefly comprises contacting the surface to be decontaminated with an alkaline solution containing an alkali and an alkanolamine and preferably also a complexing agent, then contacting the surface with an alkaline oxidizing solution which contains an alkali and a soluble permanganate, and also preferably a soluble fluoride e.g. an alkali metal fluoride, followed by treatment of the surface with an acid bath, preferably an aqueous nitric acid solution. Such process is effective for removing radioactive contaminants emitting any one or more of the forms of radiation alpha, beta or gamma.

Alloys frequently used in the construction of the loop components of nuclear reactors are cobalt alloys, and particularly those cobalt alloys designated Stellite 6 and Stellite 12 alloy. Stellite 6 is composed of 25 to 31% chromium, 3 to 6% tungsten, and the balance is cobalt. Stellite 12 is composed of 26 to 32% chromium, 6 to 10% tungsten and the balance is cobalt. In carrying out the process of my said copending application, it has been observed that the alkaline permanganate solution employed in such process is particularly corrosive to the aforementioned Stellite 6 and Stellite 12 alloys, so that treatment with such alkaline permanganate solutions results in undesirable corrosion, and particularly substantial pit corrosion, of the base metal during removal of radioactive contamination and scale deposits from component parts composed of these alloys.

It is an object of the invention to provide alkaline permanganate compositions which are substantially less corrosive to certain cobalt alloys such as Stellite 6 and 12, than are previously employed alkaline permanganate compositions.

Another object is the provision of novel alkaline permanganate compositions either in the form of a solution, or in the form of a dry powder for preparing such solution, for use in radioactive decontamination or removal of scale deposits from surfaces of cobalt alloys including Stellite 6 and 12, substantially without any pit corrosion of the base metal, and without adversely affect-

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ing the decontaminating and scale removal properties of the composition.

Still another object is the incorporation of an additive in alkaline permanganate compositions, rendering the resulting composition much less corrosive to cobalt alloys such as Stellite 6 and 12.

A still further object of the invention is to afford procedure for removing radioactive contaminants and scale deposits from cobalt alloys such as Stellite 6 and 12, without corrosion of such alloys.

These and other objects of the invention will appear hereinafter.

I have found that by adding a soluble chromate compound, e.g. alkali metal or ammonium chromate or alkali metal or ammonium dichromate, to the aforementioned alkaline permanganate solution, such solution, which in the absence of said chromate compound is corrosive to certain cobalt alloys such as Stellite 6 or 12, is thereby rendered non-corrosive to such alloys, particularly as regards freedom from pitting. This non-corrosive advantage is obtained without any sacrifice of the effectiveness of the solution for removal of radioactive contamination and scale deposits from said alloys.

While any soluble chromate or dichromate can be employed, I preferably employ sodium, potassium or ammonium chromate, or the corresponding dichromate salts. Where, for example, sodium, potassium or ammonium dichromate is employed, such dichromate is transformed in the alkaline permanganate solution to the corresponding chromate salt. Mixtures of the aforementioned soluble chromates and dichromates can be employed also. While varying amounts of the soluble chromate compound can be employed, the amount of such compound generally employed in the alkaline permanganate solution is about 0.1 to about 4.0%, preferably about 0.5 to about 2%, by weight of the solution.

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. The solution may also contain an alkali metal carbonate. The amount of alkali metal hydroxide employed may range from about 1 to 25% by weight of the solution, preferably about 10 to about 25%, the amount of permanganate from about 0.4 to about 12% by weight of the solution, preferably about 3 to about 9%, the amount of alkali metal carbonate from 0 to about 15%, usually about 5 to 15% when such carbonate is present.

A preferred type of alkaline permanganate solution is one which contains in addition to the chromate compound, a water soluble inorganic fluoride derived from any source which produces fluoride-containing ion in strong alkaline solution. The fluoride may be a simple fluoride such as the alkali metal fluorides sodium or potassium fluoride, or ammonium fluoride, or I can employ soluble bifluorides such as sodium bifluoride, or complex fluorides, such as alkali metal or ammonium fluoborates and silicofluorides. These complex fluorides decompose in the alkaline-permanganate system to produce the fluoride ion in the solution. The amount of fluoride compound which I employ in the solution is generally in the range of about 0.25 to about 8%, usually about 0.75 to about 6%, by weight of the solution. 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.

Alkali permanganate solutions containing chromate or dichromate according to the invention can be prepared by adding the components separately to water, or said solutions can be prepared by dissolving in water dry solid

compositions containing in admixture the various ingredients, namely, the alkali, the permanganate, and the chromate compound, and other optional ingredients which may be employed, such as soluble fluoride. In such solid compositions the amount of alkali metal hydroxide preferably employed is about 15 to about 85% by weight of the composition, alkali permanganate is preferably about 2 to about 45%, the amount of chromate or dichromate is about 1 to about 10%, and when used, the amount of soluble fluoride, e.g. alkali metal fluoride, is about 1 to about 15% by weight of the composition. It will be understood that where the total percentage of the aforementioned components does not total 100%, the balance of any of such solid compositions may be sodium carbonate or some other optional additive to bring the total composition to 100%. Such dry composition is generally dissolved in water in an amount in the range of about 2 ounces to about 4 pounds per gallon of water, to make up working solutions whose components are present in amounts substantially within the ranges noted above for the solution.

The temperature of treatment of the surfaces to be decontaminated or descaled in the alkaline permanganate solution of the invention is generally in the range of about 100 to about 220° F., preferably 180 to 200° F. Time of treatment is from say about 15 minutes to about 2 hours.

The chromate-containing alkaline permanganate bath of the invention aids in removal of radioactive contaminants or scale deposit, and is particularly useful when employed in conjunction with treatment of cobalt alloy components to be decontaminated and/or descaled, in the alkaline solution containing alkanolamine noted above and described in my said copending application. In preferred practice the latter alkanolamine-containing solution is first applied in treating parts to be processed for decontamination and descaling, and then the chromate-containing alkaline permanganate solution of the invention is employed, preferably followed by a third step of acid treatment with aqueous solutions, e.g. aqueous nitric acid or phosphoric acid solutions. The alkaline solution containing alkanolamine, and preferably also a complexing agent, and the aqueous acid solution employed in the process, together with temperature of treatment and other operating conditions for these solutions, are described in detail in my above-noted copending application, and reference is therefore made to said copending application for a complete description and understanding of such solutions, since they form no part of the instant invention.

The following are examples of practice of this invention.

EXAMPLE 1

The loop piping of a nuclear reactor, which is the loop for recirculation of water from the reactor to the heat exchange equipment, and composed chiefly of 304 stainless steel but having portions composed of Stellite 6 and 12, had been operating for over a year. The equipment was tested and radiation readings for 23 points in the cell averaged about 115 mr. per hour. (The term "mr." designates a milliroentgen of radiation.) The equipment was then subjected to decontamination according to the following procedure:

The loop was first treated with a 50% solution in water, designated solution A₂, of the following solution, designated solution A₁:

Solution A ₁	Wt. percent of solution
Potassium hydroxide.....	38
Triethanolamine.....	13.7
Tetra-kis N-(2-hydroxypropyl) ethylenediamine.....	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

Solution A₂ was heated to 135° C. and circulated through the loop piping for two hours.

Solution A₂ was then drained and a cold solution equivalent to 1% by volume of 42 Bé. nitric acid was circulated for 10 minutes to neutralize any remaining solution A₂, and was then drained.

A solution designated solution B₂, formed by dissolving in water a composition B₁ in a concentration of 2 lbs. per gallon, was heated to 115° C. and circulated through the loop piping for 2 hours and then drained. Composition B₁ and solution B₂ formed therefrom are given below:

	Composition B ₁ , percent by weight	Solution B ₂ , percent by weight
Potassium hydroxide.....	69.8	13.5
Sodium fluoride.....	7.4	1.43
Potassium permanganate.....	19.8	3.83
Sodium chromate.....	3.0	0.58
Water.....		80.66

The loop piping was then flushed with water, a nitric acid solution, designated solution C₁, and having a concentration equivalent to 30% by volume of 42 Bé. nitric acid, was circulated at about room temperature through the loop piping for one hour and then drained. The system was then flushed. Radiation readings for 23 points in the equipment was reduced to an average of about 3.4 mr. per hour.

It was noted that practically no corrosion or pitting of the base metal of either the stainless steel or Stellite portions of the equipment took place as result of the decontamination process.

EXAMPLE 2

The process of Example 1 is repeated using similar radioactively contaminated equipment, but employing in place of solution B₂, solution B₃, formed by dissolving in water in a concentration of 2 lbs. per gallon, a composition designated composition B₄, set forth below:

	Composition B ₃ , percent by weight	Solution B ₄ , percent by weight
Potassium hydroxide.....	72.8	14.0
Sodium fluoride.....	7.4	1.42
Potassium permanganate.....	19.8	3.8
Water.....		Balance

Treatment with solution B₃ results in substantial pit corrosion of the portions of the equipment composed of Stellite 6 and 12.

EXAMPLE 3

A series of 1" square specimens of Stellite 6 and Stellite 12 alloy covered with scale deposit and exposed to radioactive contamination were treated first in solution A₁ for about an hour at boiling temperature and then in solution B₂ under about the same conditions as to temperature and time as for solution A₁.

The specimens were then treated in solution C₁ at 30 to 40° C. for about half an hour, and then rinsed.

The parts were found to be decontaminated and descaled effectively, and the amount of corrosion or pitting of the base metal of the Stellite 6 and 12 samples was negligible, the amount of said corrosion being of the order of about 0.001 to 0.01 mil.

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EXAMPLE 4

The procedure of Example 3 is repeated using in place of solution B₂, solution B₅ set forth below:

Solution B₅

	Ounces/gal.	Percent by weight
Sodium hydroxide.....	15	8.2
Sodium carbonate.....	18	9.8
Potassium permanganate.....	8.5	4.6
Potassium dichromate.....	3	1.6
Water.....	1 gal.	75.8

Decontamination, descaling and corrosion results obtainable are similar to the results of Example 3.

EXAMPLE 5

The procedure of Example 3 is repeated using in place of solution B₂, solution B₆, noted as follows:

Solution B₆

	Ounces/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

While decontamination and descaling results are satisfactory, substantial pit corrosion of the Stellite alloy results.

EXAMPLE 6

The procedure of Example 3 is repeated, employing in place of solution B₂, solution B₇, set forth below:

Solution B₇

	Ounces/gal.	Percent by weight
Sodium hydroxide.....	15	9.8
Sodium carbonate.....	18	11.7
Potassium fluoride.....	4	2.6
Potassium permanganate.....	8.5	5.5
Potassium chromate.....	3	1.9
Water.....	1 gal.	68.5

Decontamination, descaling and corrosion results are similar to the results of Example 3.

From the foregoing, it is apparent that I have developed a composition of matter in the form of a novel alkaline permanganate solution containing a soluble chromate, and a dry powder mixture for preparing such solution, said solution being effective, particularly when used in conjunction with certain alkaline solutions containing an alkanolamine, for radioactive decontamination and descaling of the components of a nuclear reactor, which components are composed of cobalt alloys, especially those designated Stellite 6 and 12, without producing undesirable pitting or corrosion of such alloys, said pitting or corrosion generally resulting when alkaline permanganate solutions in the absence of such chromate are employed.

While I have described particular embodiments of my invention, 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:

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1. A composition of matter which when dissolved in water forms an alkaline solution suitable for decontaminating and descaling cobalt alloys without any material corrosion thereof, which consists essentially of about 15 to about 85% by weight of alkali metal hydroxide, about 2 to about 45% by weight of alkali metal permanganate, and about 1 to about 10% of a member of the group consisting of soluble chromates and dichromates.

2. A composition as defined in claim 1, wherein said member is an alkali metal chromate.

3. A composition of matter which when dissolved in water forms an alkaline solution suitable for decontaminating and descaling cobalt alloys without any material corrosion thereof, which consists essentially of about 15 to about 85% by weight of alkali metal hydroxide, about 2 to about 45% by weight of alkali metal permanganate, about 1 to about 15% of a soluble fluoride, and about 1 to about 10% of a member of the group consisting of soluble chromates and dichromates.

4. A composition as defined in claim 3, wherein said member is an alkali metal chromate and said soluble fluoride is an alkali metal fluoride.

5. An aqueous alkaline solution suitable for decontaminating and descaling cobalt alloys without any material corrosion thereof, which consists essentially of about 1 to about 25% by weight of alkali metal hydroxide, about 0.4 to about 12% of alkali metal permanganate, and about 0.1 to about 4.0% of a member of the group consisting of soluble chromates and dichromates.

6. An aqueous alkaline solution suitable for decontaminating and descaling cobalt alloys without any material corrosion thereof, which consists essentially of about 1 to about 25% by weight of alkali metal hydroxide, about 0.4 to about 12% of alkali metal permanganate, about 0.25 to about 8% of a soluble fluoride, and about 0.1 to about 4.0% of a member of the group consisting of soluble chromates and dichromates.

7. An aqueous alkaline solution as defined in claim 6, wherein said soluble fluoride is an alkali metal fluoride and said member is an alkali metal chromate.

8. An aqueous alkaline solution suitable for decontaminating and descaling cobalt alloys without any material corrosion thereof, which consists essentially of about 10 to about 25% by weight of alkali metal hydroxide, about 3 to about 9% of alkali metal permanganate, about 0.75 to about 6% of a soluble fluoride, and about 0.5 to about 2% of an alkali metal chromate.

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