June 17, 1969 T. P. SPRAGUE 3,450,576

INHIBITION OF URANIUM METAL CORROSION

Filed Oct. 20, 1965

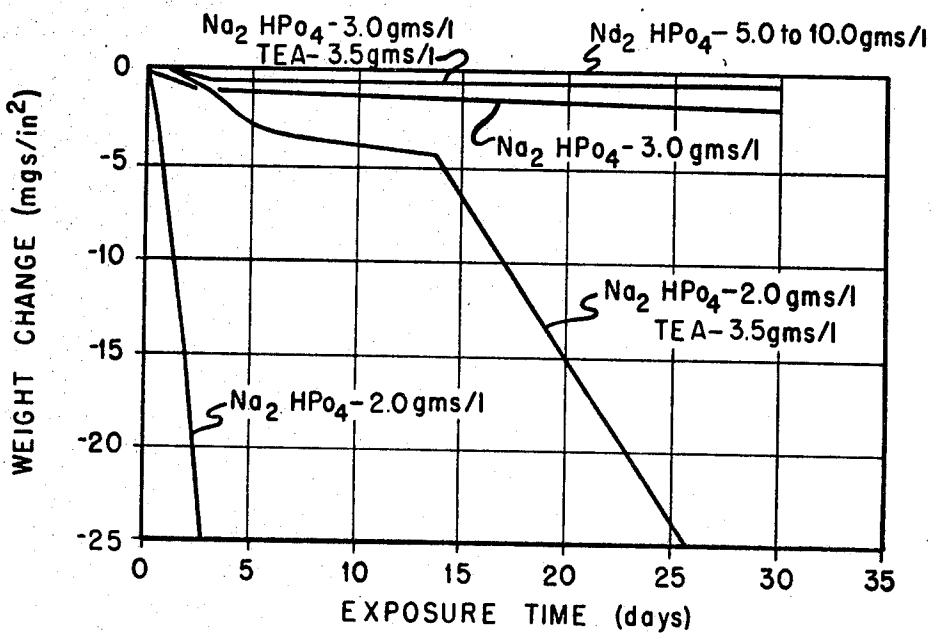


Fig. 1

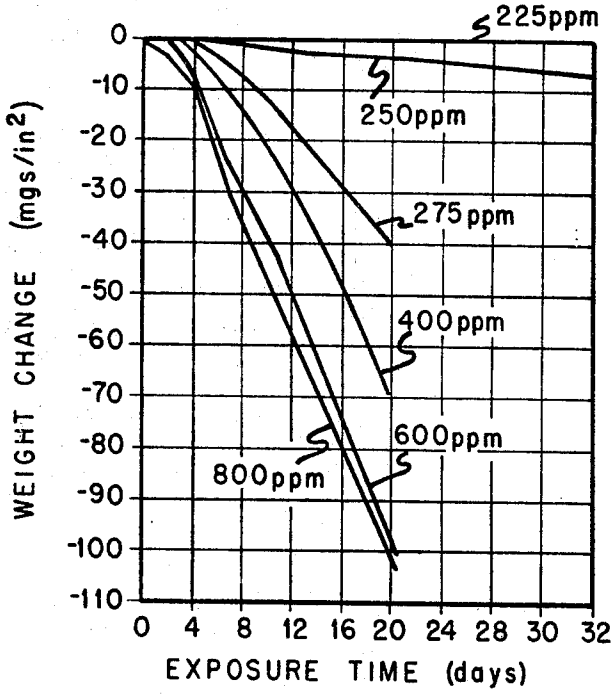


Fig. 2

INVENTOR.
Theodore P. Sprague
BY
Roland A. Anderson
ATTORNEY.

United States Patent Office

3,450,576

Patented June 17, 1969

3,450,576

INHIBITION OF URANIUM METAL CORROSION

Theodore P. Sprague, Clinton, Tenn., assignor to the United States of America as represented by the United States Atomic Energy Commission

Filed Oct. 20, 1965, Ser. No. 499,119

Int. Cl. C23f 7/10

U.S. Cl. 148—6.15

2 Claims

ABSTRACT OF THE DISCLOSURE

Uranium corrosion problems occurring during the machining of uranium metal were found to be due to the presence of chloride ions in the machining coolant. This corrosion was effectively inhibited by utilizing a machining coolant consisting of water and about 3 to 10 grams of an orthophosphate compound per liter of water.

The invention described herein was made in the course of, or under, a contract with the U.S. Atomic Energy Commission. This invention relates generally to coolants for use in machining uranium metal, and more particularly to improved aqueous coolants for such use whereby corrosion of the uranium metal due to the presence of chloride ions in the coolant is inhibited.

In machining uranium metal, the selection of a proper coolant is an important consideration from various standpoints such as, for example, tool wear, ease of metal working, production rates, health hazards, and minimization of fire hazards due to the inflammability of uranium turnings, an inherent danger in machining uranium. Significant advancements have been made in coolant technology to where true water-solution coolants, e.g., sodium nitrite-triethanolamine, have in recent times effectively replaced the previously used water-base oil emulsion type coolant due to the increased production rates attainable with water solution coolants while at the same time providing greatly reduced fire and health hazards. However, these water solution coolants suffer a significant shortcoming or drawback in that uranium metal which had been recently machined showed signs of excessive surface pitting or corrosion. Upon investigating this problem, it was determined that the uranium metal corrosion was due to the presence of chloride ions in the coolant solution. These chloride ions may be deposited in an initially chloride ion-free coolant solution in several different ways with perhaps the greatest source of chloride ions coming from surface deposits remaining on the metal after it has been annealed in a molten salt bath containing chloride. Other possible sources of chloride ions include the atmosphere surrounding the uranium metal working equipment, and perspiration from workers hands. During a typical eight-month uranium machining period, the chloride ion level in a sodium nitrite-triethanolamine coolant increased to 80 parts per million (p.p.m.), 38 percent of the nitrite had oxidized to nitrate, and the coolant had come to equilibrium with the carbon dioxide in the air. All these conditions accelerate the corrosion of uranium.

In a uranium metal machining operation using the above-mentioned previous water coolant, corrosion of the uranium metal began when the chloride content of the coolant attained a level of about 35 p.p.m. This chloride level was achieved after fusing fresh coolant for about 30 days but the attainment of this chloride level can be delayed if the uranium metal is more thoroughly washed after being annealed in the molten salt bath. Or, if desired, the coolant can be frequently changed to minimize chloride ion buildup in the coolant. However, the more thorough washing of the uranium and the frequent changing of the coolant add greatly to the cost of machining uranium.

When the chloride concentration reaches about 100 p.p.m. the corrosion of the uranium metal begins almost immediately. In other words the greater the chloride concentration in the coolant the faster the uranium metal corrodes; for example, a machined uranium part in a sodium nitrite-triethanolamine coolant corroded in about one to two weeks at a chloride concentration of about 35 p.p.m. and in about one hour at a level of about 100 p.p.m.

The present invention aims to minimize or obviate the short-comings or drawbacks of the previous true water-solution coolants by providing new water-solution coolants that are capable of protecting uranium metal from corrosion due to the presence of excessive chloride ions in the coolant. These novel results may be achieved by utilizing a coolant solution containing an orthophosphate compound or salt to substantially increase the chloride tolerance associated with uranium corrosion. For example, a dibasic sodium phosphate coolant solution may increase the chloride tolerance about 10 times over a sodium nitrite-triethanolamine type coolant.

An object of the present invention is to provide an improved coolant for use in machining uranium metal.

Another object of the present invention is to provide true-water solution coolants that are capable of protecting machine tools, coolant circulating system, retain the high production rates of the previous true water-solution coolants, and allow a higher chloride tolerance associated with uranium corrosion.

Another object of the present invention is to provide aqueous solutions with ions of orthophosphate salts to inhibit corrosion of uranium during the machining thereof.

A further object of the present invention is to provide uranium metal with a protective coating to minimize the corrosion of the uranium metal by chloride ions in machining coolants.

A still further object of the present invention is to provide essentially complete protection for uranium metal in a coolant solution containing chloride ions in a concentration of about 100 p.p.m.

Other and further objects of the invention will be obvious upon an understanding of the illustrative embodiment about to be described, or will be indicated in the appended claims, and various advantages not referred to herein will occur to one skilled in the art upon employment of the invention in practice.

In the accompanying drawing:

FIG. 1 shows data corresponding to the effect various concentrations of orthophosphates in coolant solutions have upon uranium metal corrosion; and

FIG. 2 shows data corresponding to the extent of uranium metal corrosion at various levels of chloride ion concentration in a dibasic sodium phosphate coolant solution of the present invention.

The present invention comprises the addition of small quantities of certain orthophosphates to a substantially large quantity of water to form solutions particularly adaptable for use as coolants in the machining of uranium metal. As briefly pointed out above, orthophosphate ions in uranium machining coolants provide the unique mechanism for substantially increasing the tolerance or uranium metal to the corrosive property of chloride ions in the coolants. It is believed that the phosphate ions in the

coolant solution protect the uranium metal by providing the latter with a protective coating. This coating is formed by the reaction of the phosphate ions with the uranium metal and normally appears as a thin, blue film on exposed surfaces of the uranium metal. This film has been determined by X-ray diffraction to be UO_2 and $(UO_2)_3(PO_4)_2 \cdot 4H_2O$. Also, it has been found that this film or coating is "self-healing" in that, for example, if a surface scratch through the film on a uranium metal specimen is allowed to oxidize in air and then the specimen again immersed in the phosphate solution containing chloride ions, the film will reform over the scratch to protect the underlying metal from the chloride ions.

Inasmuch as the protective film is formed on the uranium metal by the reaction of the latter with the phosphate ions (PO_4^{-3}), the particular orthophosphate compound or salt utilized to introduce a suitable number of phosphate ions in the solution is not critical. For example, successful corrosion protection has been obtained with orthophosphate salts containing a soluble metal such as sodium. Thus, for ease and clarity of description the following discussion of the invention will be directed primarily to orthophosphates containing sodium, but it is to be understood that other orthophosphates containing other soluble metals or organics, e.g., triethanolamine, may provide the desired corrosion inhibition in a manner substantially similar to orthophosphates containing sodium. However, care should be exercised in the selection of the orthophosphate compounds or salts to assure that a sufficient quantity of phosphate ions will be introduced in the solution to provide the desired film and that the other constituents of the orthophosphate do not interfere with the formation of or minimize the effectiveness of the film.

While it has been found that orthophosphate compounds or salts in the coolant solution provide the unique mechanism of forming the protective film on the uranium metal surface to give complete protection to the uranium metal from corrosion in the presence of chloride ions in concentrations of about 100 p.p.m. or less, further investigations of other phosphorous compounds did not prove as fruitful. For example, polysodium metaphosphate and sodium pyrophosphate were examined as possible coolant solution constituents but were found to provide substantially less corrosion protection than the orthophosphates, even at substantially higher concentrations.

The orthophosphate compounds tested include dibasic sodium phosphate (Na_2HPO_4) and tribasic sodium phosphate (Na_3PO_4). The solutions of each of these compounds may be formed by adding a few grams of a selected compound for each liter of water used. The particular quantities of the phosphate compound added to the water for providing adequate protection to uranium metal from chloride ion induced corrosion has been determined to be at least 3 grams per liter of water (gm./l.) and preferably about 5 gm./l. A concentration of over about 5 gm./l. does not appear to appreciably enhance the corrosion protection since in a 10-gm./l. solution containing about 100 p.p.m. chloride ions the protection afforded a uranium article appeared to be essentially the same as that in a 5-gm./l. solution containing a similar concentration of chloride ions.

In order to determine the desired quantities of phosphate in the coolant solution, aerated dibasic sodium phosphate solutions including chloride ion concentrations of 100 p.p.m. were prepared with different quantities of the orthophosphate. As shown in FIG. 1 a uranium specimen immersed in a solution having a phosphate concentration of 2.0 gm./l. showed a substantial weight change in milligrams per square inch due to corrosion in a short time period whereas uranium in a 3.0-gm./l. solution showed only a slight weight change after 30 days' immersion. On the other hand, uranium immersed in solutions having phosphate concentrations of about 5.0 to 10.0 gm./l. showed no weight change or corrosion after two months' immersion.

The addition of 3.5 gm./l. of triethanolamine (TEA) to the phosphate solutions having concentrations of 2.0 and 3.0 gm./l. provided a reduction in the amount of weight change in the uranium specimen as shown in FIG. 1. However, a similar addition of triethanolamine to the 5.0 to 10.0-gm./l. solution had no effect on corrosion inhibition.

Duplicate tests showing the effect various levels of chloride ion concentrations have upon uranium immersed in aerated solutions containing 5.0 gm./l. of dibasic sodium phosphate are shown in FIG. 2. It was found that a solution containing 225 p.p.m. of chloride ions did not show uranium corrosion in a two-month period, but that a solution containing 250 p.p.m. chloride ions pitted slightly. Solutions containing chloride ions up to 800 p.p.m. resisted attack for several hours.

The pH of the solutions of the present invention may, in part, influence the choice of the orthosphosphate compound to be used in the solution. For example, in a tribasic sodium phosphate solution the initial pH was about 12.2 with a final pH of about 9.7. This high pH would effect extensive attacks on metals such as aluminum and copper. On the other hand, a dibasic sodium phosphate solution has an initial pH of about 9.8 and a final pH of about 8.4. Thus, with these lower pH values the latter solution may be preferred. Of course, a quantity of a suitable acid, e.g., nitric acid, could be added to the solutions to further lower the pH values. If the pH of the solution is down to about 7.2, the uranium may show a slight increase in weight over a prolonged period of immersion with the uranium showing a brown color rather than the usual blue.

The corrosive effect of the phosphate-containing solutions of the present invention on metals other than the uranium that are expected to be contacted by the coolant, e.g., the metals in the uranium machining system, are of some importance. Of primary interest is cast iron which was found to be attacked significantly by the orthophosphate solutions containing chloride ions. It has been found that sodium caprylate in concentrations of at least about 5 gm./l. of solution may inhibit essentially all corrosion of the cast iron by the coolant. Yellow brass and bronze may be protected from corrosion due to contact with the coolant by adding about 10 to about 80 p.p.m. of benzotriazole to the phosphate solution. Ferrous metals, except for cast iron, were not attacked by the coolant solution.

Other orthophosphates which may be used to form uranium machining coolant solutions of the present invention include triethanolamine phosphate and sodium di-2-ethylhexylphosphate. Also, while distilled water may be preferred for forming the coolant solutions, filtered water may work satisfactorily.

It will be seen that the present invention sets forth new and improved coolant solutions particularly suitable for protecting uranium metal during the machining thereof from corrosion due to the presence of chloride ions in the coolant solution.

As various changes may be made in the form, construction and arrangement of the parts herein without departing from the spirit and scope of the invention and without sacrificing any of its advantages, it is to be understood that all matter herein is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. A uranium machining coolant comprising an aqueous solution consisting of water, about 3 to about 10 grams or orthophosphate per liter of water for inhibiting corrosion of the uranium when trace quantities of chloride are in the coolant, 5–7 grams caprylate per liter of water for inhibiting corrosion of cast iron by the coolant, and about 10–80 parts benzotriazole per million of water for inhibiting corrosion of yellow brass and bronze.

2. A method of protecting uranium metal from surface corrosion due to the presence of chloride ions in an aqueous solution used for cooling uranium metal during machining thereof, the method comprising forming a thin

film of uranium phosphate on exposed surfaces of the uranium metal by contacting the latter with a solution comprising water and phosphate ions provided by an orthophosphate in a concentration of about 3 to about 10 grams per liter of water.

References Cited

UNITED STATES PATENTS

214,360	4/1879	Brown	148—6.15
2,230,319	2/1941	Canzler	148—6.15 X
2,268,323	12/1941	Martin et al.	148—6.15
2,552,874	5/1951	Snyder et al.	148—6.15
2,692,859	10/1954	Talley	252—49.3
2,917,459	12/1959	Reamer	252—49.3
3,007,871	11/1961	Pardee et al.	252—49.3 X
3,265,620	8/1966	Heiman	252—49.3 X

FOREIGN PATENTS

644,029	10/1950	Great Britain.

OTHER REFERENCES

Mayne et al.: J. Appl. Chem. (London), vol. 10, October 1960, pp. 419–422.

RALPH S. KENDALL, *Primary Examiner.*

U.S. Cl. X.R.

83—169; 252—49.3, 49.9, 387, 394