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CHEMICAL COOLANTS FOR MACHINING
URANIUM IN THE PRESENCE OF TRACE
AMOUNTS OF CHLORIDE

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ABSTRACT

The presence of trace amounts of chloride has been found to cause severe corrosion pitting of uranium during machining operations. A dibasic sodium phosphate solution will increase the chloride tolerance approximately ten times over a sodium nitrite-triethanolamine-type coolant. In the phosphate coolant, sodium caprylate is required to retard corrosion of cast iron in the machine tools and benzotriazole to eliminate corrosion of the copper alloys in the coolant circulation system and bearings. Results indicate that bacterial protection is also required for routine use.

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INTRODUCTION

A water-base oil emulsion has been used for many years in production operations as a coolant for machining normal uranium. Recently, the change to a true water-solution coolant (sodium nitrite-triethanolamine) has resulted in increased production rates and at the same time greatly reduced fire and health hazards. However, after using the coolant for eight months severe corrosion pitting of uranium surfaces occurred on parts which had been previously annealed in a fused salt bath containing chloride. During the period of eight months, the chloride level in this coolant had increased to 80 ppm, 38% 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. It was found that better water washing of the uranium before machining and changing the coolant monthly reduced corrosion pitting considerably.

Laboratory tests have been planned to find a coolant that will protect the machine tools and circulation system, retain the high production rates of the true-solution coolants, and, at the same time, allow a higher chloride tolerance associated with uranium corrosion.

SUMMARY

Trace amounts of chloride have been found to severely corrode uranium if a true water-solution coolant is used in the machining operation. A water-soluble oil emulsion will tolerate more chloride than a true solution coolant (sodium nitrite-triethanolamine), probably because of the oily film left on the machined part. Sodium nitrite-triethanolamine corrosion pits uranium in about one hour at the 100-ppm chloride level and in about one to two weeks at the 35-ppm level.

Dibasic sodium phosphate with sodium caprylate and benzotriazole added does not show any signs of attack on uranium after two months at 225-ppm chloride, but does attack uranium at 250 ppm after one week. Chloride levels as high as 800 ppm can be tolerated for a few hours. Evidently, a film of uranium phosphate is formed on the metal which prevents the attack. The sodium caprylate is added to protect the cast iron machine tools and benzotriazole to protect the copper alloys of the coolant circulation system and bearings in the machine. Twelve commercial coolants and numerous other solutions known for their corrosion protection were tested at the 100-ppm chloride level with uranium; however, none were found to be as effective as the orthophosphate system. The commercial coolants and the more promising mixtures were tested on nine other metals or alloys that are usually found in machine tools.

Initial tests in the production area showed that some means of bacterial control is also necessary when using the phosphate solution. Initial machining tests show that the phosphate coolant performs well on uranium; however, further tests are recommended.

EXPERIMENTAL PROCEDURE AND RESULTS

SAMPLE PREPARATION

Specimen Preparation

The initial uranium test specimens (1" x 1" x 0.025") were cut from metal which had been hot rolled and annealed. Other uranium specimens were used that had been hot rolled, salt-bath annealed, and machined to 0.050 inch. An analysis of a typical test specimen is given in Table 1 and the grain structure is shown in Figure 1. The specimens were dipped in 35% nitric acid to remove surface oxide, rinsed with water and acetone, and weighed. No difference was noted in the performance of the two types of specimens. Alloys that were tested consisted of Type 1020 cold-rolled mild steel, hot-rolled mild steel, gray cast iron, vega air-hardened tool steel, oil-hardened tool steel, Type 2014F aluminum alloy, yellow brass (ASTM B-36 alloy 6), Meehanite GM (nodular cast iron), and bronze (ASTM B-144 alloy 3B). These alloys were cut into 1 by 1-inch pieces that varied in thickness from 1/8 to 1/4 inch. The surface film was removed by successive polishings to 600-grit papers.

Coolant Preparation

All commercial coolants were made up to the desired concentrations with filtered water. Special mixtures were made from reagent-grade chemicals and distilled water.

Table 1
ANALYSIS OF IMPURITIES IN URANIUM TEST SPECIMENS
(All Values in Parts Per Million)

Al	9	Li	< 0.2
As	< 10	Mg	2
Au	< 1	Mn	9
B	0.1	Mo	< 4
Ba	< 2	Na	< 1
Be	< 0.01	Nb	< 4
Bi	< 1	Ni	6
C	33	P	< 100
Ca	< 10	Pb	< 1
Cd	< 0.1	Pd	< 1
Co	< 1	Rb	< 20
Cr	2	Sb	< 2
Cu	5	Si	60
Cs	< 100	Sn	< 1
Fe	80	Sr	< 20
Ga	< 1	Ti	< 4
Ge	< 0.4	Tl	< 4
H	1.44	V	< 1
Hf	< 100	W	< 100
In	< 2	Zn	< 10
K	< 6	Zr	< 20

A 759

Figure 1. PHOTOMICROGRAPH OF A URANIUM TEST SPECIMEN.
(100X; Polarized Light)

TESTING PROCEDURE

Each sample was periodically removed from the various solutions, rinsed and scrubbed to remove any loose deposit, rinsed with acetone, and weighed. Any corrosion pitting, color changes, or precipitate formation in the solutions were also noted.

The uranium specimens were initially placed in a closed bottle. Their observed corrosion rates were much less than those experienced in production. Very low corrosion rates were also obtained when the test solution was continually dripped onto the specimens. Tests were then conducted by suspending the specimens in the test solution ($\sim 25^{\circ}\text{C}$) on a Nichrome V wire and bubbling a small stream of air around the sample using the apparatus shown in Figure 2. Figure 2 also shows (on the left) a test specimen suspended in "fresh" coolant and one in a coolant that has been used for about eight months. This method of testing increased the corrosion rate by about a factor

106388(U)

Figure 2. APPARATUS FOR DETERMINING SPECIMEN CORROSION.

of ten. Since the air-injection method more nearly simulated actual machining conditions and results, it was used in all subsequent tests on the metals. Most corrosion tests were run for two months unless the corrosion rate was found to be quite high.

Usually, because the corrosion was of the pitting type, an exact duplication of results was not obtained and only trends were noted. Also, in most cases, only single tests were made because of the large number of experiments. However, in the investigation of certain variables, duplicate and triplicate experiments were made because greater accuracy was desired.

The machining tests were conducted on a lathe by production personnel and under actual production conditions.

RESULTS AND DISCUSSION

In an attempt to determine the cause of uranium corrosion in production operations, the first experiments were run using coolants that had been used in actual machining work. Later, experiments were performed to find some coolant that would permit higher levels of chloride contamination without uranium corrosion than could be achieved with the sodium nitrite-triethanolamine coolant in general production use. The data on various coolants that were tested are given in Table 2.

Table 2
ANALYSIS OF COMMERCIAL COOLANTS

Coolant	Density(1) (gm/cc)	pH	Principal Constituents (gms/liter)				Other Constituents
			NO ₂ ⁻	TEA(2)	Cu ⁺²	CrO ₄ ⁻²	
A	0.938	-	-	-	-	-	Sulfonated Emulsible Oil
B	1.152	11.05	109	145	0.8	0	Polyethylene Glycol
C	1.228	10.90	190	313	0.8	0	
D	1.221	11.25	210	321	0	0	
E	1.080	9.55	~ 0.6	300	-	0	50.3 gms/l "Organic Acid"; Diethyleneglycol
F	1.177	10.45	151	298	0	0	Propylene Glycol; Benzotriazole
G	1.115	9.00	0	403	-	-	27 gms B/l as Borate; Propylene Glycol; Benzotriazole
H	1.057	8.30	~ 15	160	-	-	"Organic Sulfur Compound"; Propylene Glycol; Benzotriazole
I	1.233	10.7	161	335	1.26	23	
J	1.207	11.15	190	332	0	0	~ 0.7% Sodium Mercaptobenzothiazole
K	1.193	11.95	149	313	0	0	~ 0.7% Sodium Mercaptobenzothiazole 34.4 gms/l Tetrasodium Versenate
L	1.143	11.45	98	433	0	0	~ 0.7% Sodium Mercaptobenzothiazole ~ 5% Polyethylene Glycol

(1) At about 25° C.

(2) Triethanolamine.

Tests on Uranium

Water-Soluble Oil Coolants - Initially, a 5% solution of Coolant A (Table 2), an emulsible oil, was used. Although it had greater tolerance for chloride than Coolants C or D which are water soluble and replaced it, complete protection from trace amounts of chloride was not obtained, as shown by Figures 3 and 4. The amount of corrosion encountered by 100-ppm chloride in distilled water is shown in Figure 5. It was also seen that filtered water causes considerable corrosion even though the chloride was very low, while no corrosion pitting occurred with demineralized water in a ten-day period.

Commercial Coolants - Coolant B, which has had considerable use in uranium machining at various times, has approximately one half the nitrite concentration that Coolants C and D have, and is quite unsuitable for machining where there is a possibility of chloride contamination. The rates of corrosion are shown in Figure 6 and the amounts of corrosion are shown in Figure 7.

A specimen exposed to Coolant C, which has had considerable use in machining uranium, showed no signs of corrosion pitting after 30 days immersion in a solution containing no chloride, as shown in Figure 8(a). However, the addition of 100-ppm

Figure 3. URANIUM CORROSION BY AN AERATED FIVE PERCENT SOLUTION OF COOLANT "A".

chloride to Coolant C produced considerable pitting in one day, Figure 8(b), and started visible pitting about one hour after immersion. Figure 8(c) shows a much greater amount of corrosion after one day by the same coolant that had been used for machining uranium for eight months. Figure 9 shows the extensive corrosion that occurred after two months in Coolant D which is similar to Coolant C and later replaced it. A partial chemical analysis of a fresh 1% solution of Coolant C, and the coolant after use for five weeks and eight months is given in Table 3. Carbon dioxide absorbed from the air during the time the coolant was used lowered the pH as well as formed the soluble sodium uranyl carbonate. Most of the uranium that dissolved precipitated as UO_2 .

(a) 100-ppm Chloride

15274

(b) 500-ppm Chloride

15273

Figure 4. PITS OF URANIUM SPECIMENS AFTER IMMERSION FOR THIRTY DAYS IN A FIVE PERCENT SOLUTION OF COOLANT "A" AND VARIOUS AMOUNTS OF CHLORIDE. (4.5X)

Figure 5. URANIUM CORROSION IN VARIOUS TYPES OF AERATED WATER.

Figure 6. URANIUM CORROSION BY AN AERATED SOLUTION OF COOLANT "B".

(a) Two-Months Exposure; No Chloride

109400

(b) Fourteen-Days Exposure; 100 ppm Chloride

109399

Figure 7. URANIUM SPECIMENS AFTER IMMERSION IN A SOLUTION OF COOLANT "B" FOR DIFFERENT TIMES. (4X)

(a) New Solution for Thirty Days; No Chloride

106762

(b) New Solution for One Day; 100 ppm Chloride

106765

(c) Used Solution for One Day; 80 ppm Chloride

106764

Figure 8. URANIUM SPECIMENS AFTER IMMERSION IN A ONE PERCENT SOLUTION OF COOLANT "C"
FOR VARIOUS TIMES AND WITH VARIOUS AMOUNTS OF CHLORIDE. (4X)

109401

Figure 9. URANIUM SPECIMEN AFTER IMMERSION FOR TWO MONTHS IN A SOLUTION OF COOLANT "D" CONTAINING 100 PPM CHLORIDE. (4X)

Table 3
PARTIAL CHEMICAL ANALYSIS OF COOLANT C
(1% Solutions)

Substance	Used		New (gms/l)
	8 Months (gms/l)	5 Weeks (gms/l)	
HCO ₃ ⁻	3.2	2.3	-
SO ₄ ⁼	0.14	-	0.012
NO ₂ ⁻	2.2	2.2	2.3
NO ₃ ⁻	1.4	0.31	0.05
Cu ⁺⁺	0.021	-	0.008
U	1.3	0.20	0
Cl ⁻ (ppm)	80	23	< 1
pH	8.80	8.55	9.65

Considerable oxidation of the nitrite to nitrate occurred. It will be later shown that nitrate, carbonate, and copper accelerate the chloride corrosion. A comparison of Figure 10 with Figure 6 shows that Coolant C is much superior to Coolant B in the presence of chloride because of the increased nitrite concentration which it contains.

Figure 10. URANIUM CORROSION BY DIFFERENT AERATED SOLUTIONS OF COOLANT "C" AND CONTAINING VARIOUS AMOUNTS OF CHLORIDE.

Figure 10 also shows that an increase in the concentration of Coolant C reduces the amount of corrosion in the presence of chlorides. A similar effect is indicated in Figure 11 which shows that doubling the nitrite concentration nearly eliminated corrosion in a 100-ppm chloride solution, while more than doubling the triethanolamine concentration had little effect. Similar data also are shown in Figure 12 when the Coolant C, used for eight months, was diluted with both water and fresh coolant. As indicated, dilution with water left the coolant still quite corrosive because of the lowered nitrite concentration even though the chloride concentration was also lowered; dilution with fresh coolant kept the nitrite concentration at nearly the same level while reducing the chloride so that the coolant became noncorrosive with sufficient dilution.

Figure 11. URANIUM CORROSION BY AERATED COOLANT "C" CONTAINING CHLORIDE AND OTHER ADDITIVES.

Several experiments were performed to demonstrate the influence of various components of Coolant C in the presence of chloride. Figure 13 is a graph that shows the results of these tests. None of the components caused corrosion pitting in the absence of chloride. Triethanolamine by itself offered little or no protection. The presence of 2 gms/l of nitrite gave results comparable with those found for Coolant C under similar conditions, as shown when comparing Figures 10, 14, and 18. Addition of a trace of copper to the nitrite increased the rate of corrosion slightly. Addition of four moles of triethanolamine per mole of copper sulfate (21-ppm Cu and 200-ppm triethanolamine) to a solution containing two grams of nitrate per liter caused a great increase in the corrosion rate.

Figure 12. URANIUM CORROSION BY VARIOUS AERATED SOLUTIONS OF USED AND NEW COOLANT "C" WITH CHLORIDE ADDED.

Figure 13. URANIUM CORROSION BY VARIOUS AERATED CHEMICALS.

Figure 14. URANIUM CORROSION IN AERATED COOLANTS "C" AND "D" SHOWING THE EFFECT OF ADDED COPPER.

Figure 15. URANIUM CORROSION IN AERATED COOLANTS "C" AND "D" SHOWING THE EFFECT OF ADDED NITRATE. (1.35 gms/l)

Figure 16. URANIUM CORROSION BY COOLANT "C" IN EQUILIBRIUM WITH VARIOUS ATMOSPHERES. (1% Coolant C; 1.35 gms/l NO_3^- ; 0.021 gm/l Cu^{+2} ; 100 ppm Cl^-)

The role of copper in Coolants C and D was further studied, as summarized in Figure 14. As shown, a trace of copper was found to increase the rate of corrosion in the presence of chloride. As the result of these experiments, production operations were switched to the use of Coolant D which is free of copper. The same effect is noted in Figure 15. A comparison of Figures 14 and 15 show that 1.4 gms/l of nitrate greatly increase the rate of corrosion. Figure 16 shows the effect of carbon dioxide, nitrogen, and oxygen. The carbon dioxide-saturated solution shows a rapid linear rate of 31 mgs/in²/day in the presence of air. No doubt the initial slow rate in other similar curves was due to the low initial carbon dioxide concentration. Air which had been pressed through Ascarite to remove the carbon dioxide showed a much slower rate of corrosion. Extremely slow rates were found in a nitrogen atmosphere

and seemed to be rather independent of the carbon dioxide concentration. The presence of oxygen in the air increased corrosion of uranium over that found for nitrogen and this is opposite to that found by Waber(1) for distilled water at 70° C. The rate of corrosion in Coolant D with 35-ppm chloride is shown in Figure 17 at various nitrate concentrations. The rate was much less at 35-ppm chloride and required an induction period of several days. In general, the rate increased with increasing nitrate concentration. The pH of Coolant C, or 2 gms/l of nitrite solutions, was found to have no effect on uranium corrosion in the pH range of 8 to 10. An experiment in which several ions were added to Coolant C is summarized by Figure 18. As indicated, none of these show any great promise.

A number of other commercial coolants were also examined. The effect of Coolant F, which is similar to Coolant D except that the nitrite concentration is somewhat less, is shown in Figure 19. The effect of nitrate was again shown to increase the corrosion

Figure 17. URANIUM CORROSION IN AERATED COOLANT "D" SHOWING EFFECT OF NITRATE. (1% Coolant D; 35 ppm Cl⁻)

Figure 18. URANIUM CORROSION BY AERATED COOLANT "C" WITH CHLORIDE AND OTHER ADDITIVES.

rate. Coolant G, which is a triethanolamine borate, was found to be too ineffective in the presence of chloride even at high concentrations, as shown in Figure 20. Coolant E, which is very low in nitrite but contains an unidentified organic soap of triethanolamine, was found to be quite effective in the presence of chloride at high concentrations, as shown in Figures 21 and 22. Figure 23 shows that neither triethanolamine or triethanolamine and diethylene glycol were responsible for the effectiveness of Coolant E, so the organic soap which seemed to provide a good film

Figure 19. URANIUM CORROSION BY AERATED COOLANT "F".

on the uranium was probably the active agent. Coolant H, which is also quite low in nitrite but contains an organic sulfur compound, performed well at high concentrations, as shown in Figure 24. The addition of large amounts of nitrate reduced its effectiveness considerably. Its effective protection at high concentrations against chloride is undoubtedly due to the film formed on the uranium. Coolant I, which contains some chromate as well as nitrite, was found to be quite effective, as shown in Figure 25; however, more severe corrosion started after about 27 days. This coolant was not considered for routine uranium machining because of the possible industrial hygiene problems associated with the chromates. Six quite similar coolants were tested under similar conditions in triplicate. When 1% solutions were compared, Coolant D (highest in nitrite) was by far the best. When tests were made at equal nitrate concentrations, a 1.4% solution of Coolant K appeared the best; however, corrosion pitting still occurred. In both cases Coolant B, which has been used

Figure 20. URANIUM CORROSION BY AERATED COOLANT "G".

Figure 21. URANIUM CORROSION BY AERATED COOLANT "E" WITH 35 PPM CHLORIDE ADDED.

Figure 22. URANIUM CORROSION BY AERATED COOLANT "E" WITH 100 PPM CHLORIDE ADDED.

Figure 23. URANIUM CORROSION IN VARIOUS AERATED SOLUTIONS CONTAINING CHLORIDE.

Figure 24. URANIUM CORROSION IN AERATED COOLANT "H" CONTAINING CHLORIDE AND NITRATE.

Figure 25. URANIUM CORROSION IN AERATED COOLANT "I".

considerably in production operations, produced the worst conditions. The results are plotted in Figures 26 and 27.

Synthetic Coolants - A number of the more common corrosion inhibitors^(2, 3) were tested on uranium in solutions containing 100-ppm chloride at various concentrations and both with and without triethanolamine. Chromate was found to be a rather good inhibitor; however, the required concentrations would have been higher than desired for industrial hygiene control and the system was not extensively studied. The data are plotted in Figure 28. Molybdates were tested in the same manner, and graphs of the results are given in Figures 29 and 30. The molybdates are not as effective as the chromates and the addition of triethanolamine increases the effectiveness. The tungstates, shown in Figure 31, are not as good as the molybdates. Triethanolamine was found to decrease the effectiveness at low tungstate concentrations and to increase the effectiveness at higher concentrations. The same effect was found to be true with a number of the inhibitors. The molybdates and tungstates were not further considered as they are expensive coolants. Ferrocyanide solutions were also tested as they have been found to be an effective corrosion inhibitor for iron.⁽⁴⁾

Figure 26. URANIUM CORROSION IN AERATED COOLANTS CONTAINING CHLORIDE.

The data, plotted in Figure 32, show that ferrocyanide is not a good inhibitor for uranium in the presence of chloride except at very high concentrations. It was thought that triethylenediamine might be a good inhibitor; however, the results show that this is not true in the presence of chloride (Figure 33). The results of adding oleic acid to triethylenediamine, as plotted in Figure 34, indicates that this soap provides a protective film which greatly reduces the corrosion rate. The rate is further reduced with an acid/TEDA ratio of two instead of one. However, these solutions are expensive and foam badly. Therefore, an antifoaming agent would also be required.

Figure 27. URANIUM CORROSION IN AERATED COOLANTS WITH EQUAL NITRITE CONCENTRATIONS CONTAINING CHLORIDE. (2.1 gms/l NO_2^- ; 100 ppm Cl^-)

The phosphate coolants were examined quite extensively. Dibasic sodium phosphate results are shown in Figures 35 and 36. Again, poorer results were obtained with triethanolamine at low phosphate concentrations, while improved results were found at slightly higher phosphate concentrations. At a concentration of five grams of phosphate per liter, no triethanolamine was required. Even better results were obtained with the tribasic sodium phosphate, as shown in Figure 37; however, this solution could not be used because of other metals in the system, as will be shown later. Tests were also conducted on triethanolamine phosphate. The results, plotted in Figure 38, show that they were not as good as those obtained with the sodium salt. The difference may lie in the higher amine concentrations. Sodium di-2-ethylhexylphosphate was also tested and the results (Figure 39) show that a lower phosphate concentration was required than with any of the orthophosphates; however, this would

Figure 28. URANIUM CORROSION IN AERATED SODIUM CHROMATE SOLUTIONS CONTAINING CHLORIDE.

still make an expensive coolant. Figure 40 shows that polysodium metaphosphate, which is well known as an inhibitor, gave very little protection. All phosphorous compounds have been compared on a PO_4^{3-} basis whether they contain ionizable phosphate or not. Sodium pyrophosphate, as indicated in Figure 41, offered greater protection than polysodium metaphosphate, but still did not compare with the orthophosphates even at the higher concentrations. The orthophosphates were the only compounds found that gave complete protection in 100-ppm chloride solutions. An example of a uranium specimen immersed for two months in a dibasic sodium phosphate

Figure 29. URANIUM CORROSION IN AERATED SODIUM MOLYBDATE SOLUTIONS CONTAINING CHLORIDE. (1.0, 5.0, & 10.0 gms/l Molybdate)

solution is presented in Figure 42. No signs of attack were found other than a thin blue film which was determined by X-ray diffraction to be UO_2 and $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. This coating undoubtedly provides the protection. It was also found that the film is self healing. The surface was scratched, the scratches were allowed to oxidize in the air, and then the specimen was again immersed in a phosphate solution containing chloride. There was no evidence of chloride attack. Usually a slight weight gain was observed; however, this gain was less than the accuracy of the analytical balance. Microscopic examination of the uranium surface indicated very few

Figure 30. URANIUM CORROSION IN AERATED SODIUM MOLYBDATE SOLUTIONS CONTAINING CHLORIDE. (3.0, 4.0, 5.0, and 10.0 gms/l Molybdate)

thin spots while the bottom of the machining grooves appeared metallic. By comparison, uranium which had been immersed in 1% solutions of Coolants B, C, F, J, K, and L with no chloride present and for the same length of time showed a very slight weight loss which was outside the accuracy of the balance. Oxide was noted in the bottom of the machining grooves and more spots were present. Duplicate tests were made to determine the maximum chloride that could be tolerated by a solution containing five grams of PO_4^{3-} /l as the dibasic salt. It was found that a solution containing 225 ppm of chloride did not show corrosion pits in two months, but a solution containing 250-ppm Cl^- pitted slightly. Solutions containing up to 800 ppm resisted attack for several hours. The data have been plotted and the graph is presented in Figure 43. The effect of pH on uranium in the phosphate coolant was studied briefly. Uranium showed no signs of attack or weight change when immersed in a Na_3PO_4 solution for

Figure 31. URANIUM CORROSION IN AERATED SODIUM TUNGSTATE SOLUTIONS CONTAINING CHLORIDE.

two months. The initial pH was 12.2 and the final pH was 9.7. No changes were noted on uranium immersed for the same length of time in Na_2HPO_4 . The initial pH was 9.2 and the final pH was 8.4. Uranium immersed for two months in a solution at a pH of 7.2 showed a very slight weight increase and the metal was brown instead of the usual blue color. The pH of the solution remained constant.

Tests on Other Metals

Commercial Coolants - Studies were also made on the other metals usually found in the machine tools or their fixtures. A number of the commercial coolants were compared first. One percent solutions of Coolants B, C, D, and L containing 100-ppm

Figure 32. URANIUM CORROSION IN AERATED POTASSIUM FERROCYANIDE SOLUTIONS CONTAINING CHLORIDE.

chloride attacked yellow brass to some extent and bronze quite rapidly. The first three were expected to attack the copper alloys as no copper inhibitor was present; however, Coolant L was not expected to cause corrosion since this coolant was supposed to contain a copper inhibitor. Coolant B gave the most corrosion. Coolant I corroded yellow brass only slightly while Coolants F, J, and K gave no corrosion due to the copper inhibitors. Coolants B, D, F, J, K, and L containing 100-ppm chloride did not corrode cold-rolled steel; Coolants B, D, and L containing 100-ppm chloride did not corrode hot-rolled steel nor the oil and air-hardened tool steels. Gray cast iron was very slightly rusted by Coolants B, D, E, I, and L containing 100-ppm chloride. Meehanite GM was not attacked by Coolants B and L, but very slightly attacked by D. The Type 2014F aluminum alloy was only slightly tarnished by Coolants B, D, and L in the absence of chloride, with B showing the least amount of attack. The addition of 100-ppm chloride to Coolant D resulted in a rapid attack on the alloy. Uranium and the aluminum alloy were found to be the most susceptible to chloride attack.

Figure 33. URANIUM CORROSION IN AERATED TRIETHYLENE-DIAMINE SOLUTIONS CONTAINING CHLORIDE.

Figure 34. URANIUM CORROSION IN AERATED TRIETHYLENE-DIAMINE-OLEIC ACID SOLUTIONS CONTAINING CHLORIDE.

Figure 35. URANIUM CORROSION IN AERATED DIBASIC SODIUM PHOSPHATE SOLUTIONS CONTAINING CHLORIDE. (1.0, 5.0, & 10.0 gms/l Phosphate)

Phosphate Coolants - The major effort was devoted to the phosphate test coolants. Most of the test solutions had 100-ppm chloride included. The tribasic phosphate did not attack cold and hot-rolled steels nor oil and air-hardened tool steels, but pitted cast iron slightly after the pH had dropped to 9.8. Yellow brass was very slightly attacked while bronze was attacked to a greater extent. The solution very rapidly attacked Type 2014F aluminum because of the high pH. Tribasic phosphate was not further considered because of the attack on some of these metals. Dibasic sodium phosphate did not attack any of the ferrous metals except cast iron and Meehanite GM where graphitic cell corrosion⁽⁵⁾ occurred. Very little attack continued after

Figure 36. URANIUM CORROSION IN AERATED DIBASIC SODIUM PHOSPHATE SOLUTIONS CONTAINING CHLORIDE. (2.0, 3.0, 5.0, & 10.0 gms/l Phosphate)

the black graphitic residue formed; however, a bad looking surface was obtained. The phosphate solution greatly retarded the corrosion of cast iron since it corrodes rapidly and uniformly in distilled water. The absence of chloride reduced the amount of corrosion of cast iron but did not eliminate it. The addition of triethanolamine also reduced considerably the amount of corrosion of cast iron but did not eliminate it except with Meehanite GM. The addition of triethanolamine to either dibasic or tribasic phosphate also creates problems with the copper alloys, but this can be eliminated by the addition of 80-ppm sodium mercaptobenzothiazole.⁽⁶⁾ This attack is much greater with the tribasic phosphate. The aluminum alloy is sometimes slightly tarnished by the dibasic phosphate.

The work was then concentrated on finding a suitable cast iron inhibitor that was compatible with the phosphate system. Hersch, et al⁽⁴⁾ did considerable work on rust preventatives for mild steel and cast iron. They found small amounts of chromates

Figure 37. URANIUM CORROSION IN AERATED TRIBASIC SODIUM PHOSPHATE SOLUTIONS CONTAINING CHLORIDE.

to be the best inhibitor for cast iron. Experimental work in the dibasic phosphate system with 100-ppm chloride showed that the amount of corrosion was drastically reduced by chromate, but a concentration greater than 200 ppm would be required to eliminate corrosion. Concentrations of this amount could cause an industrial hygiene problem.

Phosphate ⁽¹⁾ (gms/l)	TEA (gms/l)	Chloride (ppm)
● 1.0	4.71	100
○ 2.0	11.9	100
△ { 3.0	17.8	100
5.0	23.5	100

(1) Added as H_3PO_4 .

Figure 38. URANIUM CORROSION IN AERATED TRIETHANOLAMINE-PHOSPHATE SOLUTIONS CONTAINING CHLORIDE. (Mole Ratio of TEA/ PO_4^{-3} = 3)

Ferrocyanide was found to eliminate all corrosion of cast iron at concentrations of five grams per liter. All other metals tested, except yellow brass and bronze, seemed to be quite well protected. The addition of 80 ppm of sodium mercaptobenzothiazole to the phosphate-ferrocyanide-chloride solutions protected brass and bronze for about two weeks (until the copper inhibitor precipitated as benzothiazyl disulfide) after which corrosion began. Bronze was attacked more than brass. Benzotriazole⁽⁷⁾ was also tried as an inhibitor for copper alloys in the phosphate-ferrocyanide system at 80-ppm concentration, but was not as effective as sodium mercaptobenzothiazole.

Figure 39. URANIUM CORROSION IN AERATED SODIUM DI-2-ETHYLHEXYL PHOSPHATE SOLUTIONS CONTAINING CHLORIDE. (1.0 gm/l PO_4^{-3} Equals 3.51 gms/l Sodium Di-2-ethylhexyl Phosphate)

The addition of one gram per liter of nitrite to a dibasic phosphate solution reduced but did not eliminate the amount of corrosion on cast iron, so this was not pursued further.

The sodium salts of certain organic acids were also investigated rather thoroughly by Hersch, et al.(4) They found that a seven or eight-carbon acid required a smaller concentration to prevent corrosion on mild steel and cast iron. Accordingly, tests were run with sodium valerate, caprylate, and caprate. The caprylate appeared to require the least amount for good protection of cast iron. Although the protection is not always complete, as indicated by the appearance of tiny black graphitic spots at times, the problem does not seem to be serious. Concentrations of five to seven grams per liter of sodium caprylate seemed to be adequate to control the cast iron corrosion at a very low level. Uranium, bronze, oil and air-hardened tool steels, Meehanite GM, and cold and hot-rolled steels seemed to stand up well over a two-month period. Very slight staining occurred on the Type 2014F aluminum alloy.

Figure 40. URANIUM CORROSION IN AERATED POLYSODIUM METAPHOSPHATE SOLUTIONS CONTAINING CHLORIDE.

Yellow brass was attacked to some extent. The addition of 10 - 80-ppm sodium mercaptobenzothiazole to the sodium caprylate solution stopped the attack on the brass, but the coolant attacked the bronze somewhat. The use of 10 - 80-ppm benzotriazole also stopped the attack on brass and greatly reduced the attack on bronze. Only a very slight weight gain occurred on the bronze at the 10-ppm level and the metal was still shiny.

Tests were made on cast iron in which triethanolammonium caprylate was used in place of the sodium salt, but the inhibition of the corrosion was not improved. In addition, sodium mercaptobenzothiazole was added to inhibit the attack on brass

Figure 41. URANIUM CORROSION IN AERATED SODIUM PYROPHOSPHATE SOLUTIONS CONTAINING CHLORIDE.

and bronze. Benzothiazyl disulfide precipitated from this mixture, and this would allow eventual corrosion of the brass and bronze.

Tests were made with three commercial grades of caprylic acid of 90 to 99% purity as the sodium salt on a number of different metals, and in all cases they proved satisfactory. The major impurities in the commercial acids are caproic and capric acids. Only reagent-grade dibasic sodium phosphate has been tested, but undoubtedly a cheaper grade would be satisfactory. Tests were also made using distilled water; however, filtered water could probably be used. If the precipitated magnesium and calcium phosphates proved to be troublesome in machining, they can be easily filtered out. A few tests were made using tetra-sodium versenate added to the phosphate system to stabilize the filtered water. It was found necessary to add 0.4 gm/l of the salt to stabilize the local filtered water. No attacks occurred on uranium and cold-rolled steel without the addition of other inhibitors to the sodium versenate solution; however, brass was slowly attacked due to the amine that is present in the solution.

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Figure 42. URANIUM SPECIMEN AFTER IMMERSION FOR TWO MONTHS IN DIBASIC SODIUM PHOSPHATE CONTAINING CHLORIDE. (4X; 5.0 gms/l PO_4^{-3} ; 100 ppm Chloride)

Production Machining Tests and Related Bacterial Problems

Some experimental machining tests on uranium have been made by production personnel. Although the tests were not extensive, uranium appeared to machine as well with the phosphate coolant as with the present coolant. However, it was found that bacteria existed in the production facilities that were not encountered in the laboratory and caused the coolant to become rancid in about two weeks. Some Elcide 75 was added to the coolant in the production facilities at the prescribed concentration of 0.25 oz/gal and the machining tests were conducted intermittently for over two months without any signs of rancidity. However, it was found that Elcide 75 was not too compatible with this system because insoluble brown gobules formed, yellow brass was attacked to some extent, and bronze was attacked considerably. Laboratory tests were also made with Dowicide Q; however, it was found to contain considerable free chloride so that any appreciable amount of additional chloride was sufficient to cause the uranium to pit as well as to attack the bronze slightly. It has been found that sterilization at 72° C for 15 seconds will kill the bacteria. A solution which was held at this temperature for 30 minutes was found to have no effect upon the corrosion-inhibiting properties of the solution.

A more complete evaluation of the machining properties of this coolant has been planned.

Figure 43. URANIUM CORROSION IN AERATED DIBASIC SODIUM PHOSPHATE SOLUTION CONTAINING VARIOUS AMOUNTS OF CHLORIDE. (5.0 gms/l PO_4^{3-} ; 7.0 gms/l Sodium Caprylate; 10 ppm Benzotriazole)

Humectants

There is some question whether a humectant is desired in the system. Four glycols were tested with the phosphate-caprylate solution and glycerol was found to be the best although a 5% solution was necessary to keep the solution from drying out. Diethylene glycol proved to be the next best with propylene glycol and ethylene glycol being about equally less effective. The residue left by a 0.1% solution of glycerol appeared to be softer than with no humectant added; however, both residues are readily soluble in additional coolant and do not dry to as hard a residue as the typical sodium nitrite-triethanolamine coolants.

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