DOWELL INCORPORATED

CHEMICAL RESEARCH LABORATORY REPORT

REMOVAL OF SCALE FROM A
HEAT EXCHANGE SYSTEM FOR
WESTINGHOUSE ATOMIC POWER DIVISION

AGREEMENT NO. 14-535 UNDER PRINCIPLE
CONTRACT NO. AT-11-1-GEN-14

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DOWELL INCORPORATED

Tulsa 1, Oklahoma

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W/O 43585

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by

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Purpose:

To remove a loosely adhered scale composed chiefly of magnetite, from a heat exchange system without corroding or attacking the alloys present in the equipment.

Possible Cleaning Methods Which Have Been Investigated

1. Strongly oxidizing acids such as chromic-nitric acid solutions.
2. The lithium form of highly cross-linked resins, such as sulfonated polystyrene, sulfonated phenol-formaldehyde, and sulfonated copolymers of vinyl toluene and styrene, which form colloidal dispersions in water.
3. Chelating agents, such as the lithium salt of ethylene diamine tetra-acetic acid.
4. Mixtures containing cross-linked sulfonated resins and a low concentration of mineral acid.
5. Low concentrations of mineral acids such as 1-3% sulfuric acid.
6. Weak acids such as oxalic and citric acids.
7. Simple iron complexing materials such as fluorides and citrates.
8. Inorganic lithium salts and lithium hydroxide.
9. Water soluble thickening agents such as methocellulose.
10. Water soluble dispersing agents such as polyethylene glycol.

Conclusions of Laboratory Results:

The use of a strongly oxidizing acid solution, such as a mixture of chromic acid and nitric acid was found to satisfactorily dissolve "crud" but in addition it was found to attack the alloys present in the unit. Solubilities and corrosion rates were found to increase with an increase in treating temperature, and also with an increase of either or both of the acids. The addition of benzidine or benzidine nitrate inhibitor to chromic-nitric acid solutions decreased both corrosion rates and solubility results. Contact angle measurements on coupons treated in both uninhibited and inhibited chromic-nitric acid solutions show that a water rinse will remove all reaction products from the alloy surfaces.

The method which gave the lowest corrosion rates, was one in which a water dispersion of a water swellable resin was used. The lithium form of highly cross-linked sulfonated polystyrene in a 0.25% concentration at 175°F. was found to be the most satisfactory resin of this type. Corrosion rates of the various alloys in this dispersion at 175°F. were less than 360 mg/sq.dm./mo. Generally speaking, this is 2 to 3 times as corrosive as distilled water at 175°F. The resin-water dispersion gave excellent suspension of scale particles. Contact angle measurements show a water flush completely

removes this resin from oxidized alloy surfaces. Stability tests show no tar is formed at 500°F.

Other resins which have been found to satisfactorily suspend scale are sulfonated phenol-formaldehyde, sulfonated styrene-vinyl toluene copolymers, sulfonated polystyrene-vinyl nitrile copolymer, and sulfonated styrene-latex. These resins, however, were not as effective as cleaning agents as the highly cross-linked sulfonated polystyrene.

The acid form of highly cross-linked sulfonated polystyrene, i.e. at pH 1.6, was found to be approximately twice as corrosive as the neutralized form, except in the case of SS410 where it was approximately 20 times more corrosive. This material was found to satisfactorily suspend Fe_3O_4 . Cleaning tests show this material is a more effective scale removing agent, because of its acid content, than is the neutralized form.

The lithium form of versene at a concentration of 0.30M and at reflux gave corrosion rates, to representative alloys, of less than 500 mg/sq.dm./mo. Solubility tests showed that at reflux for 16 hours 58% of an Fe_3O_4 sample was dissolved.

Mixtures containing 0.25% highly cross-linked sulfonated polystyrene and a low concentration of mineral acid, for example 0.5% sulfuric acid, gave corrosion rates at 175°F. to the representative alloys of less than 300 mg/sq.dm./mo., except in the case of SS410 which was extremely high, i.e. 35000 mg/sq.dm./mo. The acid content reduced swelling of the resin in water but this mixture was found to satisfactorily suspend Fe_3O_4 .

Low concentrations of mineral acids such as 0.33M sulfuric, 0.33M nitric acid and 5% HCl although satisfactory in some respects, were very unsatisfactory in others. Sulfuric and hydrochloric acid gave excellent solubility results but were found very corrosive to stainless steels, while 0.33M nitric acid gave very low solubility results even at reflux.

Weak acids such as oxalic and citric were found to dissolve Fe_3O_4 slowly at 175°F. Oxalic acid gave the best solubility of the weak acids tested and with the exception of SS410 and Armco 17-7 gave corrosion rates of less than 2000 mg/sq.dm./mo. In addition to the high corrosion rate of SS410 and Armco 17-7 oxalic acid has the further disadvantage of forming ferrous oxalate, a water insoluble precipitate. It may be possible to avoid this precipitate by continuously supplying fresh acid. The most satisfactory inhibitor found for inhibiting the action of oxalic acid on SS410 was by the use of 2.0% Dowell A25, 1% Quinaldine ethiodide and 1% Dowell F26. Citric acid as well as the other weak acids gave very low solubility results.

Simple iron complexing materials such as fluorides and citrates gave low solubility results even at temperatures as high as 300°F. Ammonium bifluoride gave excellent solubility results but was found to be extremely corrosive to zirconium and stainless steel.

Inorganic compounds such as lithium hydroxide, lithium tetraborate, etc., gave low solubility results.

Water soluble thickening agents such as methocellulose and polyacrylic acid

did not suspend or attack the scale.

Water soluble dispersing agents such as polyethylene glycol did not suspend the scale.

Discussion:

I. Strongly oxidizing acid solutions.

A. Benzidine inhibited.

Solutions containing mixtures of chromic and nitric acid and inhibited with benzidine or benzidine nitrate gave lower corrosion rates than uninhibited acid solutions. (See Data Table #1 and #2). The corrosion rates of chromic-nitric acid solutions inhibited with benzidine nitrate were somewhat higher than those inhibited with benzidine, however, solutions inhibited with benzidine contained a small amount of insoluble residue while those inhibited with benzidine nitrate contained no insoluble residue. The optimum amount of benzidine was found to be 0.3% as evidenced by the data in Table 2, Section B.

The corrosion rates of zirconium (oxidized in autoclaves under varying conditions) in chromic-nitric acid solutions may be found in Data Table 3 (A). The coupons in series A had a noticeably heavier oxide film than those in the other series. The higher corrosion rates of Series A were attributed to weight losses caused by mechanical removal of the oxide film. (i.e. when scrubbing the strip.) In view of this it is believed the corrosion rates of Series B more truly represent actual corrosion rates of oxidized zirconium. The corrosion rates of oxidized zirconium (Series B) which were given a two stage treatment (i.e. Stage #1 - in cleaning solution for 16 hours at 175°F. and Stage #2 - in degassed water at 600°F. for 2 weeks) may be found in Data Table #3B. It may be noted that in all cases the addition of benzidine inhibitor reduced the corrosion rate of oxidized zirconium in chromic-nitric acid solutions. Furthermore, in all cases corrosion rates of coupons exposed first to inhibited acid solutions were slightly higher in degassed water, than were those which had first been exposed to uninhibited acid solutions.

Solubility tests (See Data Tables 4 and 5) show that scales consisting primarily of magnetite are more rapidly attacked by uninhibited chromic-nitric acid solutions than by benzidine or benzidine nitrate inhibited solutions. These results also show that there is little, if any, difference between the solubility rate of solutions inhibited with 0.3% benzidine and 0.4% benzidine nitrate. From the solubility results recorded in Data Table #5 it was concluded that the optimum concentration for inhibited chromic-nitric acid solutions was 16% chromic - 3.6% nitric acids. A plot of the results recorded in Table #5 may be found in Graph #1. Plot A of this graph is a plot of % Scale Dissolved vs. % nitric acid, while plot B is a plot of % Scale Dissolved vs. % chromic acid. On comparing these two plots to each other it may be noted that generally speaking an increase in chromic acid causes a greater increase in the solubility rate than does an increase in nitric acid content.

Contact angle measurements (See Data Table 6) show that a water rinse

following treatment with inhibited chromic-nitric acid solutions will remove reaction products which remain on alloy surfaces following such a treatment. This conclusion is based on the following:

- (1) In all cases where the alloy surfaces were not rinsed the contact angles were zero.
- (2) Following a water rinse the contact angles were close to those of surfaces which were exposed only to distilled water. Contact angles following acid treatment varied somewhat from those exposed only to distilled water. These changes were attributed to the change in surface conditions of the coupons by exposure to the acid solution.

The most satisfactory procedure for preparing solutions of benzidine nitrate, chromic acid and nitric acid was found to be as follows: First benzidine nitrate was dissolved in water, then diluted nitric acid, diluted chromic acid, and sufficient water were added to give the desired final concentrations. In the case of benzidine inhibited chromic-nitric acid solutions the following procedure was found most satisfactory. Benzidine was added directly to concentrated nitric acid with agitation. Agitation was continued until the benzidine had changed from a crystalline structure to a flocculent structure (heat applied at this stage shortened the time required for this change to take place), cold, dilute chromic acid was then added followed by sufficient water to give the desired final concentration. A residue was present and gas (primarily CO_2) was slowly evolved. On heating this mixture to 175°F . the evolution of gas was increased, but subsided after about 1 hour at 175°F . The amount of nitric acid which reacted with 1 gram of benzidine may be found in Data Table #7. By use of this data it was possible to calculate the excess amount of nitric acid needed in order to end up with a benzidine inhibited chromic-nitric acid mixture of the desired concentration.

B. Uninhibited Solutions.

Uninhibited chromic-nitric acid solutions gave higher corrosion rates and solubility rates than did inhibited solutions. Corrosion rates of representative alloys in these solutions may be found in Data Table #1, while solubility results of these acids may be found in Data Table #4. The corrosion rates of couples in uninhibited chromic-nitric acid solutions may be found in Data Table #2. The corrosion rates of a Graphitar #14-Stellite #12 couple was found to be very high in uninhibited acid solutions.

Contact angle measurements (See Data Table #6) show that reaction products remaining on alloyed surfaces following treatment with uninhibited chromic-nitric acid mixtures may be removed by a water flush.

Comparative cleaning tests (See Data Table #8) on both oxidized SS410 and oxidized zirconium showed that uninhibited chromic-nitric acid solutions gave good removal of scale. It should be pointed out that in this table the "Estimation of % Scale Removed" refers to all the scale removed from the test coupon. Some of this scale was dissolved while some was "sloughed off." In the case of chromic-nitric acid solutions the amount of sloughed scale represented approximately 25% of the total scale removed. The data recorded in Data Table #9 shows that 100 milliliters of 10% chromic - 3% nitric acid solution will dissolve 2.3% grams of a synthetic scale consisting of 10.50%

$\text{Ni}(\text{OH})_2\text{H}_2\text{O}$; 18.31% Cr_2O_3 ; 71.19% Fe_3O_4 .

II. Water swellable or dispersable resins.

A. Sulfonated polystyrene

The lithium form of highly cross-linked sulfonated polystyrene (14 in Data Table #10) was found to be the most satisfactory of the agents of this type tested. This resin will be referred to as LiSPS #14 in this report. This resin being extremely water swellable forms a colloidal dispersion in water. The colloidal particles of resin carry an electrostatic charge just as do the colloidal particles of Fe_3O_4 present in the scale. As a result of these electrostatic charges on both the resin and scale particles, the scale particles may be dispersed and suspended throughout the swollen resin matrix. On circulating a water dispersion of resin past a loosely adhered iron oxide scale the agitation plus the electrostatically charged resin particles tend to "pull" or dislodge the Fe_3O_4 scale particles. Once dislodged the Fe_3O_4 particles are suspended in the resin-water dispersion and can be circulated from the unit.

The corrosion rates of the alloys, both oxidized and unoxidized in LiSPS #14 may be found in Data Table #11. By referring to this table it may be seen that the corrosion rates at 175°F. were 2 to 3 times higher in LiSPS #14 than in distilled water. In no case was evidence of pitting found. The corrosion rate of couples in this resin mixture may be found in Data Table #2.

In comparative cleaning time test LiSPS #14 was found to be the most satisfactory cleaning agent of this type (See Data Table #3). This material was found particularly effective on loosely adhered scales but did not effectively remove the more tightly adhered scale.

Contact angle measurements (See Data Table #6) were made to determine if a film of LiSPS #14 would remain on the oxidized alloy surfaces and if so, by what method could the film be removed. The results of these measurements show that any LiSPS #14 adhering to the surfaces could be removed by a water flush.

Stability tests of LiSPS #14 at a temperature of 500°F. showed that a tarry residue was not formed. No tarry residue could be found in the flask in which the tests were run. The viscosity of the LiSPS #14 solutions tested were sharply decreased by the high temperature (See Data Table #13). The appearance of the LiSPS #14 water suspension was changed, that is, the volume of dispersed resin was also decreased by the high temperature. From these results it was concluded that a 500°F. temperature causes a breakdown of the sulfonated polystyrene rather than forming a tar.

Filtration tests of LiSPS #14 show that the material forms a very tight filter cake on all filters through which it cannot pass. (See Data Table #14). In most cases back flushing the filter restored original permeability.

Viscosity measurements of LiSPS #14 at various concentrations (See Data Table #15) show that Dowell trucks can mix and pump a 1.5% LiSPS #14 solution. Thus if cleaning a 1000 gallon unit, 167 gallons of fluid in the unit would

be displaced out with 167 gallons of 1.5% LiSPS #14. After closing the unit the final dilution to 0.25% would be brought about by circulating. These results also show that the viscosity of a 0.25% LiSPS #14 mixture is 10 cps. This concentration was chosen because (1) LiSPS #14 effectively suspends Fe_3O_4 at this concentration and (2) it was thought that better agitation would result on circulating a low viscosity fluid than a higher viscosity fluid and thus would enable the cleaning solution to be more effective.

LiSPS #14 was prepared from a polystyrene having a molecular weight of 70,000 Staudinger. According to available information it is prepared by direct sulfonation using H_2SO_4 at 170-190°C. Sulfonated polystyrenes have been prepared in the laboratory using (A) polystyrene having a molecular weight of 25,000-50,000 Staudinger (B) polystyrene having a molecular weight of 50,000 Staudinger and (C) polystyrene having a molecular weight of 90,000 Staudinger. These three polystyrenes were directly sulfonated with H_2SO_4 at 170-190°C. The resultant resins were water swellable but not as much so as LiSPS #14. Fe_3O_4 suspension tests showed that the sulfonated polystyrene prepared from 90,000 Staudinger polystyrene gave the best results. Therefore additional work was done on this polystyrene. Resins were prepared in which 1 mol styrene monomer was reacted with from 1/4 to 2.0 mols H_2SO_4 . Fe_3O_4 suspension tests showed that resins in which 1 mol styrene monomer was reacted with 1-1.5 mols H_2SO_4 gave best results but the resin was not swollen to the extent that LiSPS #14 was. When using less than 1 mol H_2SO_4 the water swellability decreased while using more than 1.5 mols H_2SO_4 caused charring.

Tests to detect minute amounts of LiSPS #14 (See Data Table #16) show that a concentration of 2.5 ppm LiSPS #14 can be detected by using a dye, Quinaldine Red and a Duboscq colorimeter. The presence of the LiSPS #14 gives a purple cast to the solution. Methods which were tested and found unsatisfactory were: the use of a flame spectrophotometer, measurement of surface tension, and measurement of refractive index. The use of a conductance cell was found impractical when comparing laboratory distilled water to laboratory distilled water containing 2.5 ppm LiSPS #14, however, if the water in the unit is more pure than laboratory distilled water then this method might be practical.

B. Sulfonated Phenol-formaldehyde

Sulfonated phenol-formaldehyde resins were prepared in the laboratory. (See Data Table #17) These resins were prepared by the condensation of sulfonated phenol and formaldehyde. The most satisfactory resin was prepared using 1 mol sulfonated phenol, 1 mol formaldehyde and cooked with an acid catalyst. This resin is #33 in Data Table #10. The resin did not swell nearly as much as did LiSPS #14 although at 5% concentration at 175°F. the cleaning test results showed this to be the second most effective resin.

Corrosion rate tests on representative alloys (See Data Table #1) show that at 5% concentration, the lithium form of sulfonated phenol-formaldehyde (this material will be referred to as LiSPF #33 in this report) was 2-3 times as corrosive as 0.25% LiSPS #14. No evidence of pitting was found on the coupons.

Contact angle measurements (See Data Table #6) showed that a water flush completely removed an LiSPF #33 film from oxidized alloy surfaces.

C. Other Organic Cleaning Agents.

Corrosion rate tests results (See Data Table #11) on sulfonated polystyrene (listed in Data Table #10 as) 1, 2, 3, 5, 15, 16, 17, 18, 21, 22, 23; sulfonated styrene vinyl toluene copolymer #19 and sulfonated styrene-low divinyl benzene copolymer #20 show that these materials all give corrosion rates of less than 500 mg./sq.dm./mo. at 175°F.

Dispersion tests and cleaning tests (Data Table #10) show that the following resins suspended scale; 1, 2, 3, 5, 7, 15, 16, 17, 19, 20, 21, 22, 26, 31, 32 but were not as effective cleaning agents as either LiSPS #14 or as LiSPS #33.

Contact angle measurements (Data Table #6) show that a water flush will remove a film of resin #19 from alloy surfaces.

D. Mixtures of LiSPS #14 and Low Concentration of Mineral Acid

The tenacity with which the "crud" was adhered to the surfaces of the unit was unknown. As mentioned previously the neutralized form was not particularly effective on tightly adhered scale. In view of this it was decided that a possible alternative, should the neutralized form be less effective than desired, would be to use a mixture of LiSPS #14 and a low concentration of mineral acid such as sulfuric acid. LiSPS #14 was found to precipitate in mineral acids above 10% concentration. The presence of acid caused a decrease in the volume to which the resin swells in aqueous solutions. However, at mineral acid concentrations below 1% the resin was water swellable and would suspend Fe_3O_4 .

Corrosion rate results (See Data Table #1) showed that the addition of small amounts of sulfuric acid added to LiSPS #14 increased the corrosion rate particularly in the case of SS410 and Inconel X.

III. Chleating Agents

Chleating agents such as lithium Versene (the lithium salt of ethylene diamine tetra-acetic acid) are capable of forming water soluble, stable complexes. When reacted with a scale such as "crud" the Fe_3O_4 may be dissolved, and complexed and thus removed from the surfaces of the unit.

Solubility tests (Data Table #4) show that under static conditions at 175°F. only a small amount of Fe_3O_4 is dissolved while at reflux the majority of the Fe_3O_4 may be rendered soluble. It is thought the temperature increase from 175°F. to 212°F. cannot completely account for this sharp increase in solubility. An additional factor which should be considered is the agitation caused by reflux. Thus higher solubility should result in a unit in which the Versene solution is circulated than in one where the solution is held static.

Corrosion rate results (See Data Table #1 and #11) show that at 175°F. lithium Versene is 2 to 10 times as corrosive as LiSPS #14 while at reflux the corrosion rate is slightly higher than at 175°F.

A comparative cleaning test (Data Table #8) showed that the lithium form of

Versene was relatively ineffective for removal of scale.

IV. Low Concentrations of Mineral Acids

Low concentrations of uninhibited mineral acids such as sulfuric acid gave excellent solubility results (Data Table #4) even at temperatures as low as 125°F. Corrosion rates of representative alloys (Data Table #1) show that at 125°F. 0.33M H_2SO_4 rapidly attacks SS410, attacks Inconel X at a rather rapid rate and attacks the other representative alloys at low rates.

Nitric acid gave low solubility results (Data Table #4) even at reflux and was not checked further.

V. Weak Acids

Weak acids were investigated because being weak acids they attack alloys, generally, at a lower rate than mineral acids. The acids chosen for this phase of the problem varied in dissociation constant from 2×10^{-1} to 10^{-5} . For the dissociation constants of the acids tested see Data Table #12.

Solubility results (Data Table #18) show that oxalic acid gave the best results of the acids tested. The action of oxalic acid on Fe_3O_4 produces some water insoluble ferrous oxalate. The formation of this precipitate on Fe_3O_4 particles slowly builds up. As the precipitate builds up the dissolving action of oxalic acid slows down so that after 2 to 3 hours time the reaction almost stops. This may be avoided to a certain extent by continuously supplying fresh acid. In tests where this was done at 1/2 hour intervals the reaction of oxalic acid on synthetic scale proceeded at a rather uniform rate for at least $3\frac{1}{2}$ hours. (The test was terminated at that time.) In tests where the fresh acid was supplied at 1 hour intervals very little additional synthetic scale was dissolved in the 2nd and 3rd hours.

Corrosion results (Data Table #11) show that with the exception of SS410 and Armco 17-7 corrosion rates were less than 2000 mg./sq.dm./mo. In order to reduce the attack of oxalic acid on these alloys various inhibitors were tested (Data Table #19). These tests showed that by the use of 2.0% A25, 1% Quinaldine ethiodide and 1% F26, the attack of oxalic acid on SS410 could be reduced to about 3% of the attack of oxalic acid on SS410 with no inhibitor.

Solubilities of the other weak acids may be found in Data Table #18 and corrosion rates of some of these acids may be found in Data Table #11. Generally speaking these other weak acids attacked Fe_3O_4 at a very slow rate while corrosion rates were also low.

VI. Simple Iron Complexing Materials.

Fluorides and citrates form stable, water soluble complexes with iron ions. It was thought that these materials might dissolve Fe_3O_4 and be effective for removing scale. Solubility results (Data Table #20) show that even at temperatures up to 300°F. these materials are relatively ineffective. Ammonium bifluoride was found to dissolve Fe_3O_4 readily, but this was caused by the HF in the bifluoride rather than fluoride ion. Corrosion rates (Data Table #1) showed that ammonium bifluoride is extremely corrosive to zirconium

and stainless steel.

VII. Inorganic Compounds

Inorganic compounds such as lithium hydroxide, chloride, nitrate, etc. were found to actually dissolve very little Fe_3O_4 . For data concerning these materials refer to Data Table #21. In the remarks column dispersion refers to the break up of the synthetic scale. That is, with lithium citrate for example, the scale particles were broken down to particles sufficiently fine to pass through an asbestos filter pad 1/8" thick. Thus in those cases in which good dispersion is noted some of the weight loss was due to solubility and the remainder to the dispersion effect.

VIII. Water Soluble Thickening Agents and Dispersing Agents.

Materials of this type were found to have little if any effect on Fe_3O_4 scale. For data concerning these materials refer to Data Table #22.

Procedure:

Preparation of oxidized alloy surfaces. Coupons of the alloys were first cleaned by vigorously scrubbing with soap and a nylon brush. The coupons were then placed in an autoclave, being supported and separated by either asbestos or glass spacers. One liter of distilled water was then poured into the autoclave. In all cases the topmost coupon was sufficiently below the water level so that the coupons would be in contact with water during the oxidation stage. In most cases the coupons were oxidized at 600°F. for 72 hours. Gauge pressures varied during this period from 1400 to 1600 p.s.i. Following the oxidation stage the coupons were removed from the autoclave and stored in degassed distilled water at room temperature until used. The exceptions to this procedure were (1) SS410 - which was found to be excessively oxidized after 72 hours and was therefore treated for a 36 hour period and (2) Zirconium - the conditions under which zirconium was oxidized are listed in Data Table #3A.

Corrosion Rate Determinations. The dimensions of the coupons were measured to 0.1 mm. In the case of non-oxidized samples the coupons were vigorously scrubbed with soap and a nylon brush and rinsed in clear water. Coupons oxidized in an autoclave were brushed in clear water 5 times on each surface. The oxidized coupons were brushed with as uniform a pressure as possible. Coupons were then completely immersed in solutions at the desired temperature for a predetermined time. All tests at temperatures below 200°F. were made in screw capped bottles, while those above 200°F. were made in flasks equipped with reflux condensers. Following treatment, the coupons were again cleaned as above and dried in a 250°F. oven, cooled in a dessicator and weighed to 0.1 mg. The difference in weight was recorded and corrosion rates in mg/sq.dm./mo. were calculated. In determining the corrosion rate in fumes the only difference from the above procedure was that the coupons were suspended above the solution under test rather than immersed in it. In all tests following the final weight determination the coupons were examined for pitting.

Corrosion Couple Tests. In these tests the areas of the coupons were first

measured to 0.1 mm. Following this they were scrubbed with soap and water, dried to constant weight in a 250°F. oven and weighed to 0.1 mg. The couples were then assembled as follows: SS17-4 and Chrome plated SS17-4. Coupons of these two materials were rectangular in shape and of the same size. The two coupons were offset so that approximately one-half of one face of each of the two coupons were in direct contact with each other. The couples were clamped together (the clamps being insulated from the couple) so as to obtain a good metal to metal contact. Stellite #12 and Graphitar #14 - the stellite #12 coupons were machined to a cylindrical shape and were approximately 1/4" diameter by 1" long. The graphitar #14 coupons were rectangular blocks approximately 1/2" x 3/4" x 1 1/2". Three holes were drilled into the graphitar blocks and three of the stellite #12 cylinders were then inserted into the block. It was necessary to tap the pieces of stellite into place so that a good stellite to graphitar contact was obtained. Nitrided SS17-4 and Graphitar #14 - the nitrided SS17-4 sample was a journal having approximately 4 inches of 3/4" OD machined surface. The graphitar #14 was in the form of bearings (i.e. hollow cylinders) 3/4" I.D. x 1/2" wide. Four of the graphitar bearings were spaced at 1/2" intervals along the machined surface. Although the bearings snugly fit the journal, i.e., with no noticeable play, nevertheless the dissimilar materials in this couple were not in as tight a contact with each other as in the two preceding couples.

Once assembled the couples were completely immersed in the solution under test and air entrapped between the dissimilar materials was removed by evacuating the system. Tests were then run at the indicated temperature and time. After treatment the couples were disassembled, cleaned as before, dried and weighed to 0.1 mg. Corrosion rates were then calculated. Following the final weight determination the coupons were examined for evidence of pitting under a microscope; particular attention was paid to the areas in the immediate vicinity of the junction.

Solubility Determinations. Scale samples were weighed to 1 mg. In all cases, except at temperatures above 200°F., the sample and solution were placed in a bottle equipped with a screw cap. At temperatures from 200°F. to reflux a flask equipped with a reflux condenser was used. At temperatures above reflux the tests were run in glass containers inside a pressure bomb. Following the treatment the solution was poured into a centrifuge tube weighed to 1 mg. and centrifuged. Most of the liquid was then poured off and the sample was washed with distilled water and centrifuged again. The majority of the wash water was decanted and the centrifuge tube, containing sample, was dried in a 250°F. oven until constant weight. The tube and sample were weighed to 1 mg. The percent solubility was then calculated. This procedure was used in order to obtain true solubility results. From earlier work it was found that some of the finely divided particles of scale would pass conventional filter crucibles.

Contact Angle Measurements. All contact angle measurements were made on oxidized surfaces. Coupons were washed and brushed in clear water and placed in screw capped bottles in the solution under test. In each series of tests one coupon of each alloy (serving as a blank) was treated in de-gassed water. Following treatment the bottles were taken to a room equipped with an outside fresh air supply before opening. Fumes normally present in the laboratory have been found to cause erratic contact angle measurements. Upon opening the bottles the coupons were immediately treated as indicated

and then placed in a glass enclosed box containing a desiccant and equipped with plate glass sides. The coupons were then allowed to dry in the box at room temperature. Once dry, small droplets of distilled water were carefully placed on the coupons. A picture was taken of each droplet approximately 5 seconds after placing the droplet. From these pictures the average advancing contact angle as measured through the water phase was obtained.

Comparative Cleaning Time Tests. One surface of an oxidized 2" x 2" coupon was coated with a very viscous water, synthetic scale slurry to a depth of approximately 1/64". The coupon was partially dried at room temperature and then baked in an oven at 250°F. for at least 6 hours. It was then placed in the test cell (See Figure #1). The test cell was then carefully filled with distilled water so that no air remained in the cell. The cell was connected up as shown in Figure #1. Reservoirs #1 and #2 contained distilled water at 190°F. The pump was started and the valve to the test cell was then opened allowing circulation over the test coupon. The capacity of the pump was greater than the flow rate through the system and thus by use of the leveling device and the valve it was possible to maintain a constant flow rate through the test cell. By use of thermostatic hot plates it was possible to maintain constant temperature, i.e., 1°F., in the test cell. The surface of the test coupon was level with the surface at the baffle and a steady flow (with a minimum of turbulence) was maintained over the coupon. Distilled water was circulated, at 175°F. through the test cell, for 1/2 to 1 hour and the amount of scale removed was estimated by visual examination. The purpose of circulating water over the coupon was to remove any loose particles from the surface of the coupon. It was found that after circulating for 15-20 minutes all the loose scale was removed. The system was shut down and a portion of the distilled water in reservoir #2 was removed and replaced with sufficient concentrated cleaning solution so as to give the desired concentration when diluted with all the water in the apparatus. The pump was then started and the cleaning solution was circulated between reservoir #1 and reservoir #2. After approximately 5 minutes circulation the valve to the test cell was opened and the actual test was started. Following the test period the cleaning solution was removed by discharging it into another container and continuously adding fresh distilled water. Approximately 5 times the apparatus volume of distilled water was used in this operation. The test cell was then disassembled and the coupon was examined visually. The percent total scale removed was estimated by comparing the coupon to a blank.

Filtration Tests.

(A) Sand bed tests - a glass tube 1½" I.D. x 12", supported in a vertical position, was fitted with a rubber stopper at the bottom end. The rubber stopper had a 3/4" hole through it. A piece of 120 mesh screen was placed over the hole and a sand bed of the desired mesh size and thickness was placed on top of the screen. 200 ml. of solution was then poured into the tube. The top of the tube contained a stopper through which air, at 5 p.s.i. could be introduced into the system. Air pressure was applied until all the liquid had been forced through the sand bed. The amount of resin retained on the sand bed was estimated from (A) the thickness of the resin filter cake and (B) the viscosity of the filtrate.

(B) Micrometallic filter - This filter was placed in a 2" pipe union with

rubber gaskets on both top and bottom. The union was then tightened and placed in a vertical position. The water permeability of the filter was then found by noting the dimensions of the filter and the volume of water passed through the filter under a known hydrostatic head of pressure. Following this determination 200 mls of the solution under test was introduced into the system. Air pressure was applied for various lengths of time until all the fluid had passed the filter. The viscosity of the filtrate was then determined and the % of resin retained on the filter was estimated. The filter was then inverted and water was used to back flush the system. Approximately 1 liter of water was used in this operation. The system was then placed in its original position and the permeability of the filter was again checked according to the above mentioned procedure.

Preparation of Phenol - Formaldehyde Resins. Phenol and formaldehyde were mixed in the indicated molar ratios. The mixture was heated with agitation at 125°F. until the phenol was dissolved. Catalyst was then added with agitation. The alkaline catalyst used was 0.32 moles of a saturated solution of lithium hydroxide per mole of phenol. The acid catalyst used was 0.32 moles of a 1:10 C.P. sulfuric acid solution per mole of phenol. Following the addition of catalyst the temperature was increased to 180°F. and the mixture was cooked at this temperature until very thick, i.e., until on turning the reaction flask on its side the resin meniscus shifted only slightly in 10 seconds. Water was then added with agitation to give a final solution containing 10% resin. The resin water mixture was then neutralized to pH 5-6 and tested.

Dispersion tests - Both qualitative and quantitative tests were performed. The qualitative tests were conducted by placing 1 gram of synthetic scale in the bottom of a beaker. A water solution at 175°F. containing 0.5% dispersant was carefully added. After all tests had been at 175°F. for 1 hour, each beaker was stirred with a glass rod (10 rotations). The solutions then stood for 1/2 hour at which time the volume of dispersion was noted. In the quantitative tests a weighed amount of synthetic scale was placed in the flask. 100 ml. of the solution to be tested (previously brought to the desired temperature) was poured into the flask. The temperature was maintained for a given time. Following this the solution and residue was filtered through a weighed, controlled pore size, Gooch crucible. The crucible was dried for 2 hours in an oven and reweighed. It was dried an additional hour and reweighed. This was continued until a constant weight was recorded. The weight lost was recorded and the percent scale removed was calculated.

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TABLE #1

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(A) Corrosion Rates of Representative Oxidized Alloys in Various Solutions

Tests run 16 hours at indicated temperatures

Resin numbers refer to resins listed in Data Table #10

			Corrosion Rates in mg./sq.dm./mo.							
Cleaning Solution and Concentration	% Benzidine	Temp. °F.	Zr	SS347	SS410	SS17-4	Hard Chrome Plate	Stellite #6	Inccnel X	70-30 Cu-Ni
5% CrO ₃ - 1% HNO ₃		175	344 (1)	260	450	199	113	405	307	1650
5% CrO ₃ - 1% HNO ₃		Reflux	540 (1)	430	835		487	2290	1970	
5% CrO ₃ - 1% HNO ₃	0.3	175	63 (2)	396		40	38	133	82	478
10% CrO ₃ - 1% HNO ₃		175	442 (1)	174	950		75	1560	2400	
10% CrO ₃ - 1% HNO ₃		175	103 (2)	190	880				2300	
10% CrO ₃ - 1% HNO ₃	0.3	175	197 (2)	210	190	198	117	506	230	1261
10% CrO ₃ - 1% HNO ₃	0.3 Pyridine	175	166 (2)	530	550				790	
10% CrO ₃ - 3% HNO ₃		175	250 (1)	620	830	1420	25	1800	4070	7900
10% CrO ₃ - 3% HNO ₃	0.3	175	39 (2)	150	238	239	54	273	503	1480
10% CrO ₃ - 3% HNO ₃	0.3	175		140 (3)						
10% CrO ₃ - 3.6% HNO ₃	0.4 (5)	175		516						
12% CrO ₃ - 3.6% HNO ₃	0.4 (5)	175		923						

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Table #1 (Cont'd)

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Corrosion Rates in mg./sq.dm./mo.

Cleaning Solution and Concentration	% Benzidine	Temp. °F.	Zr	SS347	SS410	SS17-4	Hard Chrome Plate	Stellite #6	Inconel X	70-30 Cu-Ni
14% CrO ₃ - 3.6% HNO ₃	0.4 (5)	175		1460						
15% CrO ₃ - 1% HNO ₃		175	463 (1)	2350 (4)	1380		440	7600 (4)	8570	
15% CrO ₃ - 3.6% HNO ₃	0.3	175	179 (2)	1150					1480	
16% CrO ₃ - 3.6% HNO ₃	0.4 (5)	175	87 (2)	2100		630	1100	1570	2080	6000
18% CrO ₃ - 3.6% HNO ₃	0.4 (5)	175		2710						
20% CrO ₃ - 3.6% HNO ₃	0.4 (5)	175		6550						
20% CrO ₃ - 5% HNO ₃	0.3	175	207 (2)	2410					5770	
10% CrO ₃		Reflux	604 (2)	11300	2500		10500 (4)	28100	15700	
0.25% Li Form, Resin 14		175	21 (1)	194	147		49	241	114	
0.25% H Form, Resin 14, pH 1.6		175	37 (1)	94	3430		82	205	339	
0.25% Li Form, Resin 14; 0.5% H ₂ SO ₄		175	58 (1)	280	35200		75	247	1919 (4)	
0.5% Li Form, Resin 20		175	20 (1)	142	489		0			
0.5% Li Form, Resin 21		175	7 (1)	110	70		0			
5.0% Li Form, Resin 33		175	222 (1)	82	237		99	556	166	
0.33M Li Versene		175	313 (1)	550	230					
0.30M Li Versene		Reflux	620 (1)	136	783		100	185	148	

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Table #1 (Cont'd)

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Corrosion Rates in mg./sq.dm./mo.										
Cleaning Solution and Concentration	% Benzidine	Temp. °F.	Zr	SS347	SS410	SS17-4	Hard Chrome Plate	Stellite #6	Inconel X	70-30 Cu-Ni
0.33M H ₂ SO ₄		125	128 (1)	287	21100		25	290	2100	
0.33M H ₂ SO ₄		150	166 (1)				89	184	4400 (4)	
5.0% H ₂ SO ₄		175		251	30940					
0.33M NH ₄ HF ₂		175	92800 (1)	10200	89600	2400			1500	

Table #1 (Cont'd)

(B) Corrosion Rates of SS347 in Various Solutions, 175°F., 16 Hours

<u>Solution and Concentration</u>	<u>Type of Surface Exposed and Remarks</u>	<u>Corrosion Rate mg./sq.dm./mo.</u>
10% CrO ₃ - 1% H ₂ SO ₄	Oxidized coupon - no pits	250
10% CrO ₃ - 1% HNO ₃	Oxidized coupon - no pits	250
10% CrO ₃ - 3% HNO ₃	Oxidized coupon - no pits	600
10% CrO ₃ - 3% HNO ₃	Metallographical finish - no pits	850
10% CrO ₃ - 3% HNO ₃	1 side milled, 1 side ground - no pits	2000
10% CrO ₃ - 6% HNO ₃	Oxidized coupon - no pits	600
10% CrO ₃ - 6% HNO ₃	Metallographical finish - no pits	1400
10% CrO ₃ - 9% HNO ₃	Oxidized coupon - no pits	2900
10% CrO ₃ - 9% HNO ₃	Metallographical finish - no pits	2400
20% CrO ₃ - 3% HNO ₃	Oxidized coupon - no pits	9600
20% CrO ₃ - 6% HNO ₃	Oxidized coupon - no pits	19300
0.33M Trichloroacetic Acid	Machined coupon - no pits	80
0.33M H ₂ SO ₄	Machined coupon - badly pitted	27800
0.33M H ₂ SO ₄ , 0.4 A25	Machined coupon - no pits	2500
0.33M H ₃ PO ₄	Machined coupon - some pits	70
0.33M H ₃ PO ₄ , 0.4 A17	Machined coupon - trace pits	60

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Table #1 (Cont'd)

(C) Corrosion Rates of Oxidized Alloys in Fumes - 16 Hours

Cleaning Solution and Concentration	% Benzidine	Temp. °F.	Corrosion Rates in mg/sq.dm./mo.						Inconel 70-30	
			Zr	SS347	SS410	SS17-4	Hard Chrome Plate	Stellite #6	X	Cu-Ni
10% CrO ₃ - 1% HNO ₃		175	75 (1)	25	120		82	102	33	
10% CrO ₃ - 1% H ₂ SO ₄		175	50 (1)	0	91		80	34	0	
10% CrO ₃ - 0.5% H ₂ SO ₄		175	20 (1)	0	60		0	22	0	

(1) Series A Zirconium See Data Table #3A

(2) Series B Zirconium See Data Table #3A

(3) Acid inhibitor solution centrifuged to remove all insoluble inhibitor

(4) Coupon pitted

(5) Inhibited with benzidine nitrate

TABLE #2

CORROSION COUPLE TESTS

(A) Couple consisting of SS17-4 and Chrome-plated SS17-4

Area ratio - approx. equal; Temp. -175°F.; Time - 16 Hours

Couple Immersed In	Corr. Rate - mg/sq.dm./mo.		Remarks
	17-4	Chrome-plated 17-4	
0.25% Li SPS #14*	0	46	No pitting
10% CrO ₃ - 3% HNO ₃	102	201	No pitting
16% CrO ₃ - 3.6% HNO ₃ (0.4 Benzidine Nitrate)	0	38	No pitting

(B) Couple consisting of Graphitar #14 and Stellite #12

Area ratio - approx. equal; Temp. -175°F.; Time - 16 Hours

Couple Immersed In	Corr. Rate - mg/sq.dm./mo.		Remarks
	Stellite #12 Ave. 3 pieces	Graphitar #14	
0.25 Li SPS #14*	246		No pitting
5% CrO ₃ - 1% HNO ₃	10700		No pitting
10% CrO ₃ - 3% HNO ₃	134500		One piece pitted
10% CrO ₃ - 3% HNO ₃ (System Air Evacuated)	96700		No pitting
10% CrO ₃ - 3% HNO ₃ - 0.03% benzidine	87700		No pitting
10% CrO ₃ - 3% HNO ₃ - 0.1% benzidine	43000		No pitting
10% CrO ₃ - 3% HNO ₃ - 0.3% benzidine	134	2500	No pitting
16% CrO ₃ - 3.6% HNO ₃ - 0.4 benzidine nitrate	12		No pitting
20% CrO ₃ - 5% HNO ₃ - 0.3 benzidine	47000		No pitting

(C) Couple consisting of Graphitar #14 and Nitrided SS17-4

Area ratio - approx. equal; Temp. -175°F.; Time - 16 Hours

Couple Immersed In	Corr. Rate - mg/sq.dm./mo.		Remarks
	Nitrided SS17-4		
16% CrO ₃ - 3.6% HNO ₃ - 0.4% benzidine nitrate	12		Machined surface darkened where in contact with acid but no pitting

*Refers to resin #14 listed in Data Table #10

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TABLE #3

(A) Corrosion Rates of Zirconium oxidized under various conditions.

All corrosion tests ran for 16 hours at indicated temperature.

Series A - Oxidized at 600°F. for 72 hours

Series B - Oxidized at 600°F. for 36 hours

Series C - Oxidized at 500°F. for 20 hours

<u>Acid and Concentration</u>	<u>Temp. °F.</u>	<u>Corrosion Rate - mg./sq.dm./mo.</u>		
		<u>Series A</u>	<u>Series B</u>	<u>Series C</u>
5% CrO ₃ - 1% HNO ₃	175	344	81	97
5% CrO ₃ - 1% HNO ₃	Reflux	540	116	-
10% CrO ₃ - 1% HNO ₃	175	442	-	103
10% CrO ₃ - 3% HNO ₃	175	250	100	107

(B) Corrosion Rates of Oxidized Zirconium (Series B - from Table #3A)

Stage #1 - Cleaning solution for 16 hours at 175°F.; Stage #2 -

Degassed water at 600°F. for 2 weeks.

<u>Cleaning Solution</u>	<u>% Benzidine</u>	<u>Corrosion Rate - mg./sq.dm./mo.</u>	
		<u>Stage #1</u>	<u>Stage #2</u>
10% CrO ₃ - 3% HNO ₃	-	124	53
10% CrO ₃ - 3% HNO ₃	0.3	88	75
10% CrO ₃ - 1% HNO ₃	-	125	57
10% CrO ₃ - 1% HNO ₃	0.3	76	78
5% CrO ₃ - 1% HNO ₃	-	141	68
5% CrO ₃ - 1% HNO ₃	0.3	64	77
Distilled water	-	63	-

TABLE #4

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SOLUBILITY RESULTS

Strong Acids and Versene

Code to Sample: SS1-synthetic scale, (40% Magnetite, 15% Hematite, 25% Alpha Quartz, 20% Cr_2O_3);SS2-synthetic scale, (10.5% $\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$, 18.31% Cr_2O_3 , 71.19% Fe_3O_4);C - "crud", sample received approx. 11/13/53; A- Arco Crud; CP-C.P. Fe_3O_4

Concentration and Compound	Sample and Ratio of Sample to Solution	Temp. °F.	% Scale Dissolved in Hours							
			<u>1</u>	<u>2</u>	<u>4</u>	<u>6</u>	<u>8</u>	<u>16</u>	<u>24</u>	
5% CrO ₃ - 1% HNO ₃	A 1/200	175							30.0	
5% CrO ₃ - 1% HNO ₃	CP 1/200	175				10.5				
5% CrO ₃ - 1% HNO ₃	CP 1/200	Reflux							78.4	
7½% CrO ₃ - 1% HNO ₃	CP 1/200	175				23.4			53.4	
7½% CrO ₃ - 1% HNO ₃	CP 1/200	Reflux							98.0	
10% CrO ₃ - 1% HNO ₃	SS-2 1/200	175		18.0	23.0	32.0	36.0		56.0	
10% CrO ₃ - 1% HNO ₃	CP 1/200	175				42.7			72.2	
10% CrO ₃ - 1% HNO ₃	A 1/200	175							43.0	
10% CrO ₃ - 1% HNO ₃ - 0.3 Benzidine	A 1/200	175							8.0	
10% CrO ₃ - 3% HNO ₃	SS-2 1/200	175		16.8			44.0		64.0	76.0
10% CrO ₃ - 3% HNO ₃	CP 1/200	175				58.1				
10% CrO ₃ - 3% HNO ₃	CP 1/200	Reflux				98.9				
10% CrO ₃ - 3% HNO ₃	A 1/200	175							49.0	

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Table #4 (Cont'd)

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Concentration and Compound	Sample and Ratio of Sample to Solution	Temp. °F.	% Scale Dissolved in Hours						
			<u>1</u>	<u>2</u>	<u>4</u>	<u>6</u>	<u>8</u>	<u>16</u>	<u>24</u>
10% CrO ₃ - 3% HNO ₃ - 0.03 Benzidine	SS-2 1/200	175						57.0	
10% CrO ₃ - 3% HNO ₃ - 0.1 Benzidine	SS-2 1/200	175						48.0	
10% CrO ₃ - 3% HNO ₃ - 0.3 Benzidine	SS-2 1/200	175						20.0	
10% CrO ₃ - 5% HNO ₃ - 0.3 Benzidine	SS-2 1/200	175						28.0	
15% CrO ₃ - 1% HNO ₃	SS-1 1/200	175				61.6			
20% CrO ₃ - 1% HNO ₃	SS-1 1/200	175				77.6			
20% CrO ₃ - 5% HNO ₃	A 1/200	175						90.0	
20% CrO ₃ - 5% HNO ₃ - 0.3 Benzidine	SS-2 1/200	175						67.0	
5% CrO ₃ - 1% H ₂ SO ₄	CP 1/200	175				13.1			
7½% CrO ₃ - 1% H ₂ SO ₄	CP 1/200	Reflux						98.4	
7½% CrO ₃ - 1% H ₂ SO ₄	CP 1/200	175				27.6		55.9	
10% CrO ₃ - 0.5% H ₂ SO ₄	CP 1/200	175				41.7			
10% CrO ₃ - 1% H ₂ SO ₄	CP 1/200	175				45.7			
10% CrO ₃	CP 1/200	175						58.8	
10% CrO ₃	CP 1/200	Reflux						99.3	
10% CrO ₃	A 1/200	175						50.0	
0.33M HNO ₃	SS-1 1/200	Reflux				11.2			

Table #4 (Cont'd)

Concentration and Compound	Sample and Ratio of Sample to Solution	Temp. °F.	% Scale Dissolved in Hours					
			1	2	4	6	8	16
5% HNO ₃	A 1/200	175						25.0
0.33M H ₂ SO ₄	CP 1/200	125	6.6	13.3	26.9	41.4		
0.33M H ₂ SO ₄	CP 1/200	150	17.6	32.0	56.0	73.1		
0.33M H ₂ SO ₄	SS-1 1/100	150				22.0		
0.33M H ₂ SO ₄	CP 1/200	175				96.2		
0.33M H ₂ SO ₄	SS-1 1/100	175				28.4		
0.33M H ₂ SO ₄	SS-1 1/100	205				29.9		
0.33M H ₂ SO ₄	CP 1/200	Reflux				98.2		
5% H ₂ SO ₄	A 1/200	175						64.0
5% HCl	A 1/200	175						86.0
0.33M H ₃ PO ₄	CP 1/200	175				61.2*		
0.33M H ₃ PO ₄	CP 1/200	Reflux				54.5*		
0.33M Li Versene	CP 1/100	175				8.5		
0.33M Li Versene (9.65%) pH 7	CP 1/200	175				10.5		
0.33M Li Versene pH 7	SS-1 1/200	Reflux				58.8		
9.64% Versene Fe-3	CP 1/100	175				2.7		
9.64% Versene Fe-3 specific pH 6	CP 1/200	175				2.9		
9.64% Versene Fe-3 specific pH 6	CP 1/200	Reflux						5.1

*Weight gain

TABLE #5

Solubility Results

In all tests 0.4% benzidine nitrate was used as the inhibitor. Synthetic scale (10.5% $\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$, 18.3% Cr_2O_3 , 71.19% Fe_3O_4) was used in a ratio of 1 gram scale/200 mls solvent. Test conditions - Static, 16 hours at 175°F.

<u>% CrO_3</u>	<u>% HNO_3</u>			
	<u>3.0</u>	<u>3.6</u>	<u>4.2</u>	<u>4.8</u>
10	19.4	22.2	29.4	35.8
12	34.4	36.0	42.4	40.0
14	41.0	44.0	43.6	42.4
16	45.0	58.4	56.8	53.8
18	56.6	61.8	67.0	63.8
20	66.2	68.0	70.0	66.4

These data are plotted in Graph #1

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TABLE #6

CONTACT ANGLE MEASUREMENTS MADE ON OXIDIZED SURFACES

(A) Contact angle measurements of coupons treated in oxidizing acids - coupon treated at 175°F. 16 hours in cleaning solution. Water droplet placed on dried surface - advancing angle as measured through water phase.

Alloy	Treated in Distilled Water	Contact Angle measured through water phase			
		Treated in Uninhibited		Treated in 0.3% benzidine (1)	
		10% CrO ₃ - 3% HNO ₃		10% CrO ₃ - 3% HNO ₃	
		Unrinsed	H ₂ O rinsed	Unrinsed	H ₂ O rinsed
Zirconium	45	0	49	0	60
SS347	33	0	64	0	37
SS410	51	0	57	0	90
Inconel X	41	0	25	0	51
Stellite #6	60	0	51	0	60
Hard Chrome Plate	65	0	65	0	47

Alloy	Treated in Distilled Water	Treated in 10% CrO ₃ - 3% HNO ₃ - 0.3 Benzidine (2)	
		Unrinsed	H ₂ O rinsed
Zirconium	48	0	65
SS347	36	0	48
SS410	55	0	63
Inconel X	45	0	70
Stellite #6	70	0	90
Hard Chrome Plate	65	0	85

(1) benzidine dissolved first in acetone

(2) benzidine added directly to concentrated nitric acid.

Table #6 (Cont'd)

(B) Contact angle measurements of coupons treated in resin-water mixtures - all coupons treated 16 hours at 175°F. The LiOH, Li₂CrO₄, Li₂B₄O₇ follow-up treatments were made for 3 hours at 175°F. Water droplet placed on dried surface, contact angle as measured through water phase. Numbers in brackets refer to resins listed in Data Table #10.

Alloy	Treated in Distilled Water	Treated in 0.25% (14) Water Rinsed	Treated in 0.25% (14) Drained	Treated in 0.25% (14) the LiOH	Treated in 0.25% (14) then Li ₂ CrO ₄	Treated in 0.25% (14) then Li ₂ B ₄ O ₇
SS304	20°	20°	39°	65°	60°	45°
SS316	47	50	39			
SS322	36	49	29			
SS347	13	14	40	18	24	20
SS410	11	11	27	57	31	20
Carpenter 20	52	48	37			
Zirconium	13	13	24	41	38	8
Hard Chrome Plate	28	24	45	38	62	62
Stellite #1	35	53	28			
Stellite #6	55	59	32			
Monel	56	58	37			
Inconel X	40	47	35			
Graphitar	35	43	36			

Table #6 (Cont'd)

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<u>Alloy</u>	<u>Treated in Distilled Water</u>	<u>Treated in 0.25% (19) Water Rinsed</u>	<u>Treated in 0.25% (19) Drained</u>	<u>Treated in 0.25% (19) the LiOH</u>	<u>Treated in 0.25% (19) then Li_2CrO_4</u>	<u>Treated in 0.25% (19) then $\text{Li}_2\text{B}_4\text{O}_7$</u>
SS304	16°	11°	24°	18°	26°	17°
SS347	12	12	25	14	25	30
SS410	10	14	23	15	15	23
Zirconium	12	14	17	18	23	19
Hard Chrome Plate	27	26	33	20	23	23

Table #6 (Cont'd)

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<u>Alloy</u>	<u>Treated in Distilled Water</u>	<u>Treated in 5% (33) Water Rinsed</u>	<u>Treated in 5% (33) Drained</u>
SS304	31 ^o	29 ^o	0
SS322	46	48	0
SS347	31	37	0
SS410	31	31	0
Carpenter 20	39	40	0
Stellite #1	41	42	0
Stellite #6	61	62	0
Hard Chrome Plate	38	33	0
Inconel X	51	53	0
Zirconium	26	30	0
Graphitar	30	38	0

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TABLE #7

Determination of the amount of HNO_3 required to react with 1 gm. benzidine.

<u>Solution Under Test</u>	<u>Ratio of gms. HNO_3 reacted per gm. benzidine³</u>
50 ml. CP HNO_3 - 1 gm. benzidine	2.15/1
50 ml. CP HNO_3 - 3 gm. benzidine	2.13/1

TABLE #8

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COMPARATIVE CLEANING TIME TEST

(A) Oxidized SS410 coupons prepared with a 1/64" synthetic scale. SS-1 (40% Fe_3O_4 , 15% Fe_2O_3 , 25% SiO_2 , 20% Cr_2O_7) used in all tests.

Coupon	Stage No.	Solution	Time in Hours	Temp. °F.	Rate of fluid flow thru system	Rate of flow over coupon	Estimation of % scale removed
A	1	Water	2	175	104 ml/sec.	7.85 cm/sec.	2
	2	0.25% H SPS #14 pH 1.6 (1)	6	175	104 ml/sec.	7.85 cm/sec.	65
B	1	Water	2	175	104 ml/sec.	7.85 cm/sec.	2
	2	0.25% H SPS #14 (2)	2½	175	104 ml/sec.	7.85 cm/sec.	25
C	1	Water	1	175	72.5 ml/sec.	5.47 cm/sec.	2
	2	10% CrO_3	3	175	72.5 ml/sec.	5.47 cm/sec.	50
D	1	Water	2	175	104 ml/sec.	7.85 cm/sec.	5
	2	0.25 Li SPS #14	3	175	104 ml/sec.	7.85 cm/sec.	20
E	1	Water	1	175	72.5 ml/sec.	5.47 cm/sec.	2
	2	0.33M Li Versene	4	175	72.5 ml/sec.	5.47 cm/sec.	20
F	1	Water	1	175	104 ml/sec.	7.85 cm/sec.	2
	2	5% CrO_3 - 1% HNO_3	6	190	104 ml/sec.	7.85 cm/sec.	20
G	1	Water	1	175	104 ml/sec.	7.85 cm/sec.	2
	2	10% CrO_3 - 1% HNO_3	4	175	104 ml/sec.	7.85 cm/sec.	60

Table #8 (Cont'd)

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(B) Oxidized Zirconium (500°F. for 20 hours) (3) 1/64" synthetic scale. SS-2 (10.5% Ni(OH)₂ H₂O; 18.31% Cr₂O₃; 71.19% Fe₃O₄) used in all tests. Temp. 175°F.; Flow rate - 104 ml/sec. through system or 7.85 cm/sec. over coupon.

Coupon	Stage No.	Solution	Time in Hours	Estimation of % Scale Removed
1	1	Water	1	15
	2	10% CrO ₃ - 3% HNO ₃	3	75
2	1	Water	1	15
	2	0.25 HSPS #14 pH 1.6 (1)	3	25
3	1	Water	1	15
	2	Li OH at pH 10 (4)	24	25

- (1) pH maintained at 1.6 for duration of test by continuously adding H₂SO₄;
- (2) Original pH 1.6; after 1 hour's time pH had increased to 5;
- (3) Series C Data Table #3 (A);
- (4) pH maintained at 10 for duration of test by continuously adding LiOH.

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TABLE #9

Solubility Determination - Temp. 175°F; 5 gms. synthetic scale #2 (10.50% $\text{NiOH}_2 \cdot \text{H}_2\text{O}$; 18.31% Cr_2O_3 ; 71.19% Fe_3O_4) per 100 mls. acid solution.

SolutionGrams Scale Required to Spend Acid100 ml. 10% CrO_3 - 3% HNO_3

2.38

TABLE #10

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LIST OF ORGANIC CLEANING AGENTS WHICH HAVE BEEN TESTED

All H form resins neutralized with lithium to pH 7 for dispersion tests. Volume measurements made after standing static for 24 hours at 175°F. Concentration picked so that viscosity was 10-20 cps. Cleaning ability tests 2 hours at 175°F.

Number	Name	Type	Conc.	Dispersion Tests	Cleaning Test % Scale Removed
				% of Total Volume Occupied by Dispersed Resin	
1	Styrex M28, H form	Sulfonated polystyrene	0.5%	33	25
2	Styrex 666, H form	Sulfonated polystyrene	0.5%	66	25
3	Styrex 8, H form	Sulfonated polystyrene	0.5%	66	25
4	Polystyrene sulfonated Ref. L2121-11	Sulfonated polystyrene	0.5%	10	
5	Styrex 3, H form	Sulfonated polystyrene	0.5%	20	25
6	Polystyrene Na Sulfonate L2121-10B	Sulfonated polystyrene	0.5%	0	
7	Sulfonated polystyrene 200-400 mesh	Sulfonated polystyrene	0.5%	50	
8	SS69, H form SPS 36	Sulfonated polystyrene	0.5%	0	
9	Exp. Resin X-778 L2712-4-SS150	Sulfonated polystyrene	0.5%	10	
10	Exp. Resin X-778 L2619-44-SS139	Sulfonated polystyrene	0.5%	10	

Table #10 (Cont'd)

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Number	Name	Type	Conc.	Dispersion Tests	Cleaning Test % Scale Removed
				% of Total Volume Occupied by Dispersed Resin	
11	Pentadecyl Phenol- formaldehyde lithium sulfonate	Phenol-formaldehyde	0.5%	0	
12	Pentadecyl Phenol- formaldehyde lithium sulfonate	Phenol-formaldehyde	1.0%	0	
13	Exp. Resin 2507	Sulfonated polystyrene	0.5%	10	
14	H form 1800 Visc. SPS 36	Sulfonated polystyrene			
15	H form 4000 Visc. SPS 36	Sulfonated polystyrene	0.125%	40	33
16	H form SPS 36 (200,000 MW)	Sulfonated polystyrene	0.5%	40	33
17	H form 100 Visc. SPS 50 VT 100	Sulfonated polystyrene Vinyl Toluene Copolymer	0.5%	0	
18	H form 44000 Visc. SPS 99	Sulfonated polystyrene	0.5%	0	
19	Exp. Resin X2514 P79-99-31A	Na salt of sulfonated 75% styrene-25% vinyl toluene copolymer	0.25%	60	25
20	Colloidal Dowex 50, X 0.25	H form sulfonated styrene low divinyl benzene copolymer	0.5%	33	10

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Table #10 (Cont'd)

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Number	Name	Type	Conc.	Dispersion Tests	Cleaning Test % Scale Removed
				% of Total Volume Occupied by Dispersed Resin	
21	Exp. Resin P114-3-60	Na salt sulfonated polystyrene	0.07%	66	33
22	Exp. Resin X-2514 P79-96-25F	Na salt sulfonated	0.17%	33	10
23	Exp. Resin X-2507 P79-97-47A	H form sulfonated polystyrene	0.5%	10	
24	Exp. Resin X2514	Na salt of sulfonated polyvinyl toluene- styrene copolymer	0.5%	10	
25	H form 25 visc. SPS-VCN	H form sulfonated polystyrene vinyl nitrile copolymer	0.25%	5	
26	H form 1360 visc. SPS-VCN	H form sulfonated polystyrene vinyl nitrile copolymer	0.09%	66	25
27	Dowex 50, X4	H form sulfonated polystyrene low divinyl benzene copolymer	0.5%	2	
28	Dowex 50, colloidal	H form sulfonated styrene-divinyl benzene copolymer	0.5%	1	
29	Lustrex X-710	Ammonium form sulfonated polystyrene (Monsanto)	0.5%	5	
30	Lustrex X-770	Ammonium form sulfonated polystyrene (Monsanto)	0.5%	5	

Table #10 (Cont'd)

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Number	Name	Type	Conc.	Dispersion Tests	Cleaning Test % Scale Removed
				% of Total Volume Occupied by Dispersed Resin	
31	Dow Resin X-2524 L3060-27-SS349 (raw dried)	H form sulfonated styrene latex	0.2%	50	10
32	Dow Resin X-2524 L3060-27-SS349 (ether purified)	H form sulfonated styrene-latex	0.08%	50	10
33	Phenol-formaldehyde	1M Phenol-1M formalde- hyde acid catalyst	5.0%	33	50
34	Polyacrylic acid		0.5%	0	
35	Acrylic Acid - divinyl benzene		0.5%	1	
36	Sulfonated naphthyl- amine formaldehyde		0.5%	0	
37	SO ₂ -acrylic acid- vinyl N-butyl ether copolymer		0.5%	5	
38	SO ₂ -acrylic acid-vinyl ethyl ether copolymer		0.5%	5	
39	SO ₂ -acrylic acid-vinyl N-butyl cellulose copolymer		0.5%	5	
40	SO ₂ -acrylic acid-vinyl 2-methoxy ethyl ether copolymer		0.5%	5	

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TABLE #11

CORROSION RATES OF VARIOUS ALLOYS IN VARIOUS SOLUTIONS

16 hour tests at 175°F. Numbers in column headings refer to resins listed in Data Table 10. The pH of all H⁺ form resins was adjusted to pH 7 with LiOH. (Ox.) refers to coupons which were oxidized in the autoclaves for 72 hours at 600°F. Dissociation constants of weak acids are listed in Table #12

Alloy	Corrosion Rate in Mg/sq.dm./mo.										
	Distilled Water	0.25% (14)	0.125% (15)	0.5% (16)	0.5% (17)	0.5% (18)	0.5% (5)	0.5% (3)	0.5% (2)	0.25% (19)	0.25% (20)
SS304	66	111	116	114		46	13	31	10	0	
SS304 (ox.)	0	0								34	61
SS316	48	25	20	0	30	18	53	100	122	0	
SS316 (ox.)		100									
SS322	42	212	169	27	7	0	40	18	5	0	
SS322 (ox.)		290									
SS347	132	130	0	0		134				0	
SS347 (ox.)	137	194								133	142
SS410	10	24	18	10	16	0	117	65	50	0	
SS410 (ox.)	47	147								54	489
Armco 17-7	51	95	102	287		64	20	51	48	0	
Armco 17-7 (ox.)		127									
Carpenter 10	96	7	35	46	26	91	119	125	120	0	
Carpenter 10 (ox.)		93									
Carpenter 20	55	17	71	15	15	0	17	74	94	0	
Carpenter 20 (ox.)		58									
Stellite #1	123	319	283	439		190	94	52	282	0	
Stellite #1 (ox.)		358									
Stellite #6	44	204	188	345		157	131	114	252	125	
Stellite #6 (ox.)		241									
Stellite #19	37	100	0	0	109	0				0	
Stellite #21	17	33	10	23		84	47	21			
Stellite #21 (ox.)		105									
Colmonoy 4	202	119	223	358		244	296			268	
Colmonoy 6	52	147	102	396		356	149			15	
Monel	94	68	54	72	61	41	0	22	231	115	
Monel (ox.)		209									

Table #11 (Cont'd)

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Alloy	Distilled Water	Corrosion Rate in Mg/sq.dm./mo.									
		0.25% (14)	0.125% (15)	0.5% (16)	0.5% (17)	0.5% (18)	0.5% (5)	0.5% (3)	0.5% (2)	0.25% (19)	0.25% (20)
Inconel X	41	127	46	30	21	0	41	116	12	0	
Inconel X (ox.)		114									
70-30 CuNi	327	151	100	126		277					
70-30 CuNi (ox.)		303									
Hard Chrome Plate	54	38	0	283		0		185	69	0	
Hard Chrome Plate (ox.)	66	49								0	0
Zr (ox.) (1)	63	21								32	20

Alloy	At Reflux		0.33M (3%)		2 Hours 1%		2 Hours 0.1%		0.33M Sulfamic Acid		0.33M Acetic Acid	
	0.25% (21)	0.5% (22)	0.5% (23)	0.5% (1)	0.5% (7)	Oxalic Acid	Oxalic Acid	Oxalic Acid	Oxalic Acid	Oxalic Acid	Oxalic Acid	Oxalic Acid
SS304		36				185					23	
SS304 (ox.)	8					78	861	673	12266		53	
SS316						35					0	
SS316 (ox.)						220						
SS322						381					0	
SS322 (ox.)						2004						
SS347												
SS347 (ox.)	110					22	1516	1126	179		304	
SS410		43	41	89	128	95044	6043	5103	102773		89	
SS410 (ox.)	70					101815					39	
Armco 17-7						4279					0	
Armco 17-7 (ox.)						1145						
Carpenter 10						350					0	
Carpenter 10 (ox.)						wt. gain						
Carpenter 20						864					118	
Carpenter 20 (ox.)						215						
Stellite #1						533					158	
Stellite #1 (ox.)												
Stellite #6						365					94	
Stellite #6 (ox.)						440						

Table #11 (Cont'd)

Alloy	0.25% (21)	At Reflux 0.5% (22)	0.5% (23)	0.5% (1)	0.5% (7)	0.33M (3%) Oxalic Acid	2 Hours 1% Oxalic Acid	2 Hours 0.1% Oxalic Acid	0.33M Sulfamic Acid	0.33M Acetic Acid
Stellite #19		12				238				0
Stellite #21						209				0
Stellite #21 (ox.)						148				
Colmonoy 4						614				856
Colmonoy 6						505				549
Monel		117	115	0	118	1034				1767
Monel (ox.)						903				
Inconel X						627				124
Inconel X (ox.)						874				
70-30 CuNi						1161				1135
70-30 CuNi (ox.)						wt. gain				
Hard Chrome Plate										
Hard Chrome Plate(ox.)	0					0	0	0	175	207
Zr (ox.) (1)	7	97		96	60	112	577	401	72	75

Alloy	0.33M Formic Acid	0.33M Chloro- Acetic Acid	0.33M Phos- phoric Acid	0.25M LiOH	0.5M Li ₂ B ₄ O ₇	5% Li Citrate at Reflux	5% Li Versene at Reflux	5% Li Versene Fe-3 at Reflux
SS304				89	0	530		
SS304 (ox.)	0	107						
SS316				55	0			
SS316 (ox.)				0	0			
SS322				0	0			
SS322 (ox.)				0	0			
SS347				0	0			
SS347 (ox.)	225	367	222					
SS410				0	0	292	267	219
SS410 (ox.)	225	37470						
Armco 17-7				0	0			
Armco 17-7 (ox.)								
Carpenter 10				0	15			

Table #11 (Cont'd)

Alloy	0.33M Formic Acid	0.33M Chloro- Acetic Acid	0.33M Phos- phoric Acid	0.25M LiOH	0.5M Li ₂ B ₄ O ₇	5% Li Citrate at Reflux	5% Li Versene at Reflux	5% Li Versene Fe-3 at Reflux
Carpenter 10 (ox.)								
Carpenter 20				0	0			
Carpenter 20 (ox.)								
Stellite #1				0	0			
Stellite #1 (ox.)								
Stellite #6				0	0			
Stellite #6 (ox.)								
Stellite #19				0	63	489		
Stellite #21				21	0			
Stellite #21 (ox.)								
Colmonoy 4				29	254			
Colmonoy 6				59	162			
Monel				0	0	892		
Monel (ox.)								
Inconel X				88	0			
Inconel X (ox.)								
70-30 CuNi				126	0			
70-30 CuNi (ox.)								
Hard Chrome Plate				19	0			
Hard Chrome Plate(ox)	86	334	0					
Zr (ox.) (1)	87	71	53					

(1) Series A Zirconium See Data Table #3A

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TABLE #12

Dissociation Constants of Weak Acids at 25°C. (As taken from Lange's 'Handbook of Chemistry').

<u>Acid</u>	<u>1st H⁺</u>	<u>2nd H⁺</u>	<u>3rd H⁺</u>
Trichloroacetic Acid	1.3×10^{-1}		
Oxalic Acid	6.5×10^{-2}	6.1×10^{-5}	
Dichloroacetic Acid	5×10^{-2}		
Maleic Acid	1.0×10^{-2}	5.5×10^{-7}	
Phosphoric Acid	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Chloroacetic Acid	1.4×10^{-3}		
Tartaric Acid	9.6×10^{-4}	2.9×10^{-5}	
Citric Acid	8.7×10^{-4}	1.8×10^{-5}	4×10^{-6}
Lactic Acid	1.4×10^{-4}		
Acetic Acid	1.8×10^{-5}		

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TABLE #13

Results of Stability Tests Made on Li SPS #14 at 500°F.

- A. No visual evidence of tar on glass containers in which the tests were made.
- B. Viscosity at 80°F. as measured with Brookfield viscosimeter.

<u>Solution</u>	<u>Original Viscosity</u>	<u>Viscosity after Exposure to 500°F. for 16 Hours</u>
0.5 Li SPS #14	22	5
1.0 Li SPS #14	410	8

- C. Appearance of Li SPS #14 - water suspension after standing 24 hours.

<u>Solution</u>	<u>Original Appearance</u>	<u>After Exposure to 500°F. for 16 Hours</u>
0.5% Li SPS #14	Top 1/5 clear, colorless Lower 4/5 uniformly cloudy	Top 9/10 clear, yellowish Lower 1/10 uniformly cloudy
1.0% Li SPS #14	Top 1/10 clear, colorless Lower 9/10 uniformly cloudy	Top 4/5 clear, yellowish Lower 1/5 uniformly cloudy

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TABLE #14

FILTRATION TESTS

A. Sand bed test results - Round sand, 200 ml. 0.25% Li SPS #14 used in all tests

<u>Particle Size</u>	<u>Calculated Pore Size</u>	<u>Thickness of Bed</u>	<u>Estimated % Resin Retained on Bed</u>
20-40	60-120 microns	1"	All through
60-80	25-36 microns	1/4"	25-50%
60-80	25-36 microns	1/2"	90%
80-140	15-25 microns	1/4"	95-100%

B. Micrometallic filter - 200 ml. fluid; the numbers in the solution column refer to resins as listed in Table #10; all solutions were neutralized to pH 7 with LiOH.

<u>Solution</u>	<u>Orig. Visc.</u>	<u>Pressure psi</u>	<u>Time Held</u>	<u>Pressure</u>	<u>ML Through</u>	<u>Filtrate Viscosity</u>	<u>Estimated % Retained on Filter</u>
0.5 Li, #17	16 cps.	5	10 minutes		10	6 cps.	
		10	10 minutes		50	8 cps.	
		20	3 minutes		140	16 cps.	10-15%
0.25 Li SPS, #14	10 cps.	5	20 minutes		200	2 cps.	95%
0.5% Li SPS, #20	12 cps.	5	20 minutes		200	3 cps.	95%
0.09% Li, #26	15 cps.	5	20 minutes		200	3 cps.	95%
0.08% Li, #32	14 cps.	5	20 minutes		200	3 cps.	95%

C. Micrometallic filter - Fe_3O_4 suspended in 0.25% Li SPS #14. Fe_3O_4 had been ground and passed through the filter in a water slurry. At 100³psi 100 ml. fluid passed filter in 45 minutes. No Fe_3O_4 passed filter. On back flushing the filter the permeability was found slightly lower than originally.

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TABLE #15

Viscosity vs. Concentration - Li SPS #14

<u>Concentration</u>	<u>Viscosity in Centipoises</u>
10.0%	Very stiff paste
5.0%	Very stiff paste
2.5%	Pasty - very thick
1.5%	1440
1.0%	420
0.5%	20
0.25%	10

TABLE #16

Results of various methods tested to determine which method was most satisfactory for the detection of minute amounts of Li SPS #14.

A. Using 0.1% Quinaldine Red dye and Duboscq colorimeter it was found possible to readily distinguish between (1) 0.1% Quinaldine Red distilled water solution diluted one thousand fold and (2) 0.1% Quinaldine Red - 0.25% Li SPS #14 - distilled water solution diluted one thousand fold.

B. Using Leads and Northrup Conductance bridge and cell.- Temp. 120°F.

<u>Conc. and Solution</u>	<u>Resistivity</u>
2500 ppm Li SPS #14	0.87×10^{-3} mhos
2.5 ppm Li SPS #14	3.93×10^{-6} mhos
freshly boiled dist. H ₂ O	4.00×10^{-6} mhos

C. Using DuNoy Tensionmeter

<u>Solution</u>	<u>Surface Tension at 80°F.</u>
Distilled water	72 dynes/cm
0.25% Li SPS #14	65 dynes/cm
0.025% Li SPS #14	72 dynes/cm

D. Using Refractometer

<u>Solution</u>	<u>Refractive Index</u>
Distilled water	1.34
0.025% Li SPS #14	1.33

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TABLE #17

Results of tests made on sulfonated phenol-formaldehyde resins prepared in the Laboratory.

<u>Molar Ratio of Resin</u>		<u>Catalyst</u>	<u>Remarks</u>
<u>M Phenol</u>	<u>M Formaldehyde</u>		
1.0	1.0	Acid	Swells in H ₂ O, suspended scale.
1.0	1.0	Alkaline	Completely water soluble - did not suspend scale.
1.0	1.2	Acid	Very slight swelling in water.
1.0	1.2	Alkaline	Very slight swelling in water.
1.0	1.4	Acid	Practically no swelling in H ₂ O
1.0	1.4	Alkaline	Practically no swelling in H ₂ O

TABLE #18

SOLUBILITY RESULTS - WEAK ACIDS

Code to Sample: SS1 - Synthetic scale (40% magnetite, 15% hematite, 25% alpha quartz, 20% Cr_2O_3)
 C - "crud" sample received approximately 11/13/53, CP-C.P. Fe_3O_4

Concentration & Acid	Sample & Ratio of Sample to Solution	Temp. °F.	% Dissolved in Hours								
			0.5	1	1.5	2	2.5	3	3.5	6	16
0.33M Citric (1)	SS 1/25	175		4.0		6.0					
0.33M Citric	SS 1/25	205		6.3							
0.33M Tartaric	SS 1/25	175		3.0							
0.33M Tartaric	SS 1/25	205		4.7							
0.33M Lactic (1)	SS 1/25	175		4.0		5.0					
0.33M Lactic	SS 1/25	205		4.0							
0.33M Oxalic (1)	SS 1/25	175		15.0		18.0		20.0			
0.33M Oxalic (2)	SS 1/25	175	7.0	14.0	17.0	23.0	27.0	32.0	37.0		
0.33M Oxalic	SS 1/25	205		16.7							
0.33M Acetic (1)	SS 1/25	175		4.0		5.0					
0.33M Chloroacetic	SS 1/25	175		2.0							
0.33M Chloroacetic	SS 1/25	205	0.0	0.6							
0.33M Phosphoric (1)	SS 1/25	175		4.0							
0.5M Hydrofluoric	SS 1/25	205		12.1							

Table #13 (Cont'd)

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Concentration & Acid	Sample & Ratio of Sample to Solution	Temp. °F.	% Dissolved in Hours								
			0.5	1	1.5	2	2.5	3	3.5	6	16
0.33M Dichloroacetic	CP 1/200	175								7.3	
0.33M Trichloroacetic	CP 1/200	175								8.0	
0.33M Trichloroacetic	CP 1/200	Reflux									10.0
0.33M Sulfamic	C 1/25	175		6.8							
0.66M Sulfamic	C 1/25	175		8.7							
0.33M Sulfamic	SS 1/25	205		4.3							
0.33M Maleic (1)	C 1/25	175		5.3		5.9					
0.33M Chromic (1)	C 1/25	175		6.9		9.2					
0.66M Chromic (1)	C 1/25	175		7.8		12.4					

- (1) Acid replaced by fresh acid at 1 hour intervals
 (2) Acid replaced by fresh acid at 1/2 hour intervals

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TABLE #19

CORROSION RATES OF SS410 IN 0.33M OXALIC ACID 16 HOURS AT 175°F.

<u>Inhibitor & Concentration</u>	<u>%F26</u>	<u>Corrosion Rate Mg/sq.dm/mo.</u>	<u>Remarks</u>
None	-	105600	Heavy yellow film on coupon
2.0% Dowell A25	-	7600	Light film, easily removed
2.0% Dowell A25	0.05	7800	Light film, easily removed
2.0% Dowell A25	0.10	7900	Light film, easily removed
2.0% Dowell A25	0.50	7300	Light film, easily removed
2.0% Dowell A25	1.00	6900	Light film, easily removed
2.0% Dowell A25, 1.0% Quinaldine Ethiodide	0.5	3900	Light film difficult to remove
2.0% Dowell A25, 1.0% Quinaldine Ethiodide	1.0	3100	Light film, difficult to remove
2.0% Dowell A25, 0.4% Dowell A31	1.0	7900	Light film, difficult to remove
1.0% Dowell A25, 0.2% Dowell A31	1.0	7100	Light film, difficult to remove
2.0% Dowell A25, 0.4% Formaldehyde	1.0	7700	Light film, difficult to remove
0.4% Dowell A25		24900	Light film, difficult to remove
2.0% Dowell A12	0.05	8900	Some yellow film, easily removed
0.4% Dowell A12		16500	Tarry residue
2.0% Dowell A10	0.05	68100	Heavy film, difficult to remove
1.0% Dowell A13	0.05	78100	Heavy film, difficult to remove
1.0% Dowell A16	0.05	66900	Heavy film, difficult to remove
0.1% Dowell A17		95900	Heavy film, difficult to remove

Table #19 (Cont'd)

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<u>Inhibitor & Concentration</u>	<u>%F26</u>	<u>Corrosion Rate</u> <u>Mg/sq.dm/mo.</u>	<u>Remarks</u>
1.0% Dowell A21	0.05	62400	Heavy film, difficult to remove
1.0% Dowell A22	0.05	101500	Heavy film, difficult to remove
2.0% Dowell A22	0.05	80200	Heavy film, difficult to remove
1.0% Dowell A23	0.05	24200	Some film, difficult to remove
2.0% Dowell A23	0.05	21100	Some film, difficult to remove
1.0% Dowell A24	0.05	63900	Heavy film, difficult to remove
2.0% Dowell A26	0.05	88400	Heavy film, difficult to remove
1.0% Dowell A27	0.05	19800	Some film, difficult to remove
2.0% Dowell A27	0.05	21300	Some film, difficult to remove
0.025% Dowell A30		72900	
0.2% Dowell A31	0.05	13300	Some film, easily removed
0.4% Dowell A31	0.05	8800	Some film, easily removed
0.4% Dowell A31	1.00	7100	Some film, easily removed
2.0% Dowell A31	0.05	8600	Some film, easily removed
0.4% Dowell A31, 1.0% Quinaldine Ethiodide	0.5	7600	Light film, difficult to remove
0.4% Dowell A31, 0.4% Formaldehyde	1.0	9100	Light film, easily removed
1.0% Quinaldine Ethiodide	0.05	14300	Some film, difficult to remove
2.0% Quinaldine Ethiodide	0.05	11100	Some film, difficult to remove
0.4% Rodine 102		75300	
0.4% Carbide & Carbon 230-RD-85		75800	
0.4% Formaldehyde		102700	
2.0% Gum Tragacanth	0.05	79600	Heavy film, difficult to remove

Table #19 (Cont'd)

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<u>Inhibitor & Concentration</u>	<u>%F26</u>	<u>Corrosion Rate</u> <u>Mg/sq.dm/mo.</u>	<u>Remarks</u>
2.0% Agar	0.05	106600	Heavy film, difficult to remove
1.0% Sodium Benzoate	0.05		
1.0% Quinaldine Acid	0.05	71100	
1.0% Acridine	0.05	82400	
1.0% Dicyclohexylamine	0.05	82600	
1.0% Steric Acid	0.05	89400	
1.0% Naphthenic Acid	0.05	89800	
0.4% 15-18 coal tar bases	0.05	78500	Heavy film, very difficult to remove
1.0% 15-18 coal tar bases	0.05	58500	Heavy film, very difficult to remove
1.0% 20-30 coal tar bases	0.05	6900	Heavy film, very difficult to remove

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TABLE #20

SOLUBILITY RESULTS

Salts and Lithium Compounds. Synthetic scale (40% magnetite, 15% hematite, 25% alpha quartz, 20% Cr_2O_3) used in all tests.

Concentration and Compound	Ratio of Sample to Solution	Temp. °F.	% Dissolved in Hours		
			1 hr.	3 hrs.	6 hrs.
0.33M Li Citrate	1/25	205	2.2	4.2	
0.33M Li Citrate	1/100	205		7.3	8.3
0.66M Li Citrate	1/100	205		7.4	9.5
0.33M Li Citrate	1/50	270		5.7	
0.33M Li Citrate	1/50	300		3.5	3.3
0.66M Li Citrate	1/50	300		5.8	5.4
0.33M Li Tartrate	1/25	205	1.9		
0.33M Li Tartrate	1/100	205		3.9	
0.33M Li Tartrate	1/100	205		4.8	5.0
0.33M Li Lactate	1/25	205	1.9		
0.33M Li Lactate	1/25	205		2.9	
0.33M Li Lactate	1/100	205		4.7	
0.33M Li Lactate	1/50	300		3.8	
0.33M Li Oxalate	1/25	205	0.8		
0.33M Li Oxalate	1/25	205		2.3	
0.33M Li Oxalate	1/100	205		3.1	
0.76M $(\text{NH}_4)_2\text{HPO}_4$	1/50	300		2.9	1.5
0.33M NH_4HF_2	1/100	150			45.3
0.33M NH_4HF_2	1/100	175			51.2
0.33M NH_4HF_2	1/100	205			52.1
0.33M NH_4HF_2	1/25	175			10.0
0.33M NH_4HF_2	1/200	175			76.2

<u>Concentration and Compound</u>	<u>Ratio of Sample to Solution</u>	<u>Temp. °F.</u>	<u>% Dissolved in Hours</u>		
			<u>1 hr.</u>	<u>3 hrs.</u>	<u>6 hrs.</u>
0.66M NH_4HF_2	1/100	150			67.4
0.66M NH_4HF_2	1/100	175			69.3
0.66M NH_4HF_2	1/100	205			70.9
0.66M NH_4HF_2	1/25	175			25.0
0.66M NH_4HF_2	1/200	175			90.7
0.33M NaF	1/100	175			1.1
0.33M NaF	1/100	205			3.5
0.165M $(\text{NaPO}_4)_6$	1/100	175			16.5

TABLE #21

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RESULTS OF QUANTATIVE DISPERSION TESTS

Synthetic Scale #1 (40% Fe_3O_4 , 15% Fe_2O_3 , 25% SiO_2 , 20% Cr_2O_3) was used in all cases. A ratio of 1 gram scale/100 ml solution was used. Temp. 175°F. for 16 hours.

<u>Material Used</u>	<u>Concentration</u>		<u>% Wgt. Lost</u>	<u>Reflux Time</u>	<u>Remarks</u>
	<u>% Wgt.</u>	<u>M/l</u>			
Water	--	--	0.01	16 hrs.	
Li formate	1.3	0.25	2.40	16 hrs.	v. sl. dispersion
Li formate	3.8	0.78	2.10	16 hrs.	v. sl. dispersion
Li formate	5.0	0.96	2.49	16 hrs.	v. sl. dispersion
Li citrate	5.0	0.177	10.72	16 hrs.	good dispersion
Li citrate	5.0	0.177	11.65	44 hrs.	good dispersion
Li citrate	7.05	0.25	6.8	16 hrs.	good dispersion
Li citrate	22.0	0.78	9.3	16 hrs.	good dispersion
Li versene	5.0	0.158	11.29	16 hrs.	good dispersion
Li versene	5.0	0.158	26.7	44 hrs.	good dispersion
Li versene Fe-3 specific	1.7		20.53	16 hrs.	good dispersion
Li tartrate	4.5	0.25	2.30	16 hrs.	v. sl. dispersion
Li tartrate	14.05	0.78	3.75	16 hrs.	v. sl. dispersion
Li oxalate	2.54	0.25	0.80	16 hrs.	v. sl. dispersion
Li chloride	1.06	0.25	2.30	16 hrs.	v. sl. dispersion
Li chloride	3.30	0.78	3.75	16 hrs.	v. sl. dispersion
Li nitrate	1.72	0.25	1.3	16 hrs.	v. sl. dispersion
Li nitrate	5.38	0.78	0.9	16 hrs.	v. sl. dispersion
Li sulfate	2.74	0.25	2.8	16 hrs.	v. sl. dispersion
Li sulfate	8.57	0.78	2.1	16 hrs.	v. sl. dispersion
Li hydroxide	0.60	0.25	15.0	16 hrs.	v. sl. dispersion
Li hydroxide	1.87	0.78	9.1	16 hrs.	v. sl. dispersion

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TABLE #22

RESULTS OF QUALITATIVE DISPERSION TESTS

Synthetic scale #1 (40% Fe_3O_4 , 15% Fe_2O_3 , 25% SiO_2 , 20% Cr_2O_3) was used in all cases in a ratio of 1 gram scale/100 ml solution. Solutions at 175°F., stirred with stirring rod, allowed to stand static for 1/2 hour after which the appearance of the solution was noted.

<u>Agent</u>	<u>% Used</u>	<u>Appearance of Solution</u>
Li SPS #1	0.1	Slightly cloudy-mostly settled
Li SPS #1	0.2	Slightly cloudy-mostly settled
Li SPS #1	0.3	Cloudy - some settled
Li SPS #1	0.4	Quite cloudy-some settled
Li SPS #1	0.5	Very cloudy-some settled
Li SPS #1	0.6	Very cloudy-some settled
Li SPS #1	1.0	Very cloudy-some settled
Tamol N (Na salt of condensed amyl sulfonic acid)	0.5	Cloudy-some dispersion
Methycellulose	0.5	Slightly cloudy-slight dispersion
Collodial Li Dowex 50	0.5	Slightly cloudy-practically no dispersion
Arquad S (Soya trimethyl ammonium chloride)	0.5	Very slightly cloudy-practically no dispersion
Antarox A200 (polyethoxy-alkyl phenol)	0.5	Practically no dispersion
Polyglycol P400 (polypropylene glycol)	0.5	Practically no dispersion
Polyethylene glycol 600	0.5	Practically no dispersion
Pluronic L64 (propylene oxide - ethylene oxide condensate)	0.5	Practically no dispersion
Pluronic F68 (propylene oxide - ethylene oxide condensate)	0.5	Practically no dispersion
Carbowax 1000W (polyethylene glycol)	0.5	Practically no dispersion
Carbowax 6000W (polyethylene glycol)	0.5	Practically no dispersion

Table #22 (Cont'd)

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<u>Agent</u>	<u>% Used</u>	<u>Appearance of Solution</u>
Tergitol XC (alkyl ether of polyglycol)	0.5	Practically no dispersion
Aquaness OX 13-5000VR-1 (ethylene & propylene oxide condensed with VR-1 acid)	0.5	Practically no dispersion
Water		No dispersion

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