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EFFECT OF ZINC ION ON CORROSION OF 2S ALUMINUM, TYPE 347,
AND SAE-1020 STEEL IN STATIC WATER AT 500F

by

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May, 1956

Operated by The University of Chicago
under
Contract W-31-109-eng-38

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EFFECT OF ZINC ION ON CORROSION OF 2S ALUMINUM, TYPE 347, AND SAE-1020 STEEL IN STATIC WATER AT 500F

by
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ABSTRACT

A series of tests were made to evaluate the influence of zinc ion on the corrosion behavior of Type 347 stainless steel, 2S aluminum and SAE-1020 steel in static water at 500F.

Liberal composite tabular-pictorial data show various sources of zinc ion -- zinc acetate, commercial pigment (Kadox), hydroxide, nitrate, silicofluoride, carbonate, and zinc metal -- to be particularly effective for Type 347 in oxygenated water, slightly enhanced in hydrogenated water, partially effective for 2S aluminum, and relatively insignificant in the case of SAE-1020 steel as corrosion inhibitors.

I. INTRODUCTION

Earlier investigations⁽¹⁾ had established that appreciable amounts of corrosion products, chiefly Fe_3O_4 , were generated (for the most part) from fabrication debris, transported and deposited in critical areas of stainless steel systems in which water at 500F was recirculating. The problem was partially resolved by the use of filters to remove the debris; however, some magnetite still formed on the walls of the system piping and eventually served as a source of transportable corrosion products.

The desire to eliminate the formation of steady-state corrosion products, as well as the need for reducing corrosion damage to metals in the system, prompted a series of tests to evaluate the influence of inhibitors on the corrosive environment. Hydrogen was used originally, with satisfactory results; however, the advantages of an alternate method stimulated further tests with chemical additives.

Although the test program involved evaluation of numerous combinations of materials and additives, the scope of this report is limited to tests and observations on the most promising inhibitor, namely, zinc ion, and its influence on the corrosion behavior of commercial grade Type 347 stainless steel, 2S aluminum, and SAE-1020 steel, in an environment of current interest to reactor design engineers.

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II. THEORY

A. General

Any metal may corrode by two superficial mechanisms. In one, there are discrete areas of inhomogeneity, such as the stressed areas or impurities which provide areas of a different potential compared to the rest of the surface. Localized attack may occur also, which leads to pitting. In other cases over-all oxide formation may occur. Gradually the oxide layer thickens if the process is not self-limiting. Since the oxide usually has a higher specific volume than the metal on which it is formed, the layer is in a state of compression. If the thickening process continues, the buildup of stress will crack the film or, alternatively, the oxide which was in a state of compression will recrystallize abruptly and will assume its normal lattice dimensions. (2) In either case the layer cracks and exposes the base metal to fresh attack. The attack may be aggravated by the presence of the oxide which is cathodic to the exposed metal surface. This type of scaling is common on mild steels and even stainless steel in water at elevated temperatures.

The following is a simplified version of the theory on which the work was originally based.

In high-temperature water corrosion of stainless steel and of iron, the corrosion product is predominantly Fe_3O_4 . Several possible mechanisms may be postulated for these reactions.

The mechanism shown schematically in Fig. 1 is one in which oxygen, as such, is considered to be absent. The scheme assumes the presence of a very thin film of oxide previously formed. The dominant ions present in the aqueous phase are H^+ and OH^- , arising from the dissociation of water.

FIG. 1
OXIDATION OF IRON TO Fe_3O_4 BY HYDROGEN EVOLUTION MECHANISM

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Electrons liberated in the oxidation of the iron:

travel through the thin oxide layer to react with an H^+ to yield atomic H or free radical hydrogen:

The over-all reaction may be represented by:

a case of electron transfer. In the latter equation, the H^+ ion is acting as an oxidizing agent. It is this reaction that sets up an energy gradient to make the reaction go to the right. The Fe^{++} forms hydrated ferrous oxide, or ferrous hydroxide, $\text{Fe}(\text{OH})_2$, which is disproportionated (see Fig. 1) according to one of the following over-all reactions:

or

The scheme in Fig. 1 postulates the hydrated ferrous oxide only as an intermediate. Pfeil⁽³⁾ has shown that even at elevated temperatures a thin layer of ferric oxide overlies the magnetite layer.

Uhlig⁽⁴⁾ has postulated that in the case of stainless steel the chromium, if present in critical percentage ($\sim 12\%$), will fill out its 3d shell by picking up electrons from adjacent iron atoms and converting them to the ferric form.

According to the present hypothesis, the ferric oxide may react in the following fashion:

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At the instant the Fe^{++} is formed, it is actually a fully hydrated ion which undergoes "olation" readily, that is, the replacement of coordinated H_2O by $(\text{OH})^-$. Such compounds may lose water by dehydration as follows:

Subsequent olations and dehydrations will produce $\text{FeO}(\text{OH})$, which is not protective. However, if an inhibitor, e.g., chromate, is present, then we may expect the following:

Similarly, all of the other H_2O groups may be considered to be replaced by stable linkages utilizing the chromate to link with other iron ions. A large polymeric molecule would be formed. This molecule may be expected to have low electronic conductivity and to block the access of $(\text{OH})^-$ to other iron ions; hence, the Fe^{++} will not migrate outward and the surface will be polarized.

If the foregoing is substantially true, then other acidic, amphoteric, and even basic ions, may act to form the large molecular complex oxides which we call an inhibited oxide. The criterion of inhibitive activity is the ability of an ion to stop the thickening of the oxide layer.

It was reasoned that, if ferric ions are present, ZnO could act similarly, according to the reaction:

which would continue until all OH groups were reacted.

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B. Theory of Inhibition by Zinc Ion

The possible use of zinc ion as an inhibitor of corrosion for ordinary steels was suggested as far back as 1881 by Parker.⁽⁵⁾ Evans⁽⁶⁾ showed that drops of zinc sulfate (0.1 N) appreciably reduced the formation of rust on steel plates. A grayish-buff to brown deposit was formed, the heavier deposit forming in areas of highest oxygen concentration (cathodic region). Removal of the deposit with NaOH solution disclosed a bright surface of the base metal. Thornhill,⁽⁷⁾ working with tap water at room temperature, observed that zinc sulfate, in the concentration range of 0.0033 to 0.01 molar, reduced the corrosion of steel plates by approximately 40 to 80%. While some rust formed on top of a gray film, the latter (presumably zinc hydroxide) served as a protective barrier against further attack. More recently, Cross and Hackerman⁽⁸⁾ demonstrated, by means of the Pearson Null Bridge, that zinc ion is a purely cathodic inhibitor for SAE-1020 steel.

It is notable that in all of the cases cited above there is a retardation of attack on the metal at low temperatures; equally significant is the formation of fairly thick oxide layers which appear to stifle the reaction. In fact Evans⁽⁶⁾ states that it is impossible to keep iron bright in water dosed solely with a cathodic inhibitor. By contrast, anodic inhibitors, e.g., sodium silicate or chromates, when used in sufficient concentration, will leave a surface bright and shiny.

Where purely "oxygen-type" corrosion is involved, i.e., where the presence or absence of oxygen influences the corrosion process markedly, anodic inhibitors are most efficient. Where "hydrogen-type" corrosion is involved, i.e., the evolution of hydrogen by metal acting in an acid medium, cathodic inhibitors are better. Pickling inhibitors of the amine types are typical of the latter.

Under the conditions used in this work, zinc seems to undergo a different mechanism; no thick oxide layers form and in every way the zinc seems to behave as an anodic inhibitor.

It has been indicated that a hydrogen-evolution type of corrosion prevails at elevated temperatures. If this is true, as it is in the case of iron metal, there is less likelihood that zinc oxide would be an effective inhibitor since, at most, coordination numbers of four are involved (Fe^{++} and Zn^{++}) and probably a linear structure would result.

In the previously proposed chemical mechanism, the reaction of ZnO was postulated as a replacement of hydroxyl groups or H_2O between two hydrous (or hydrated) ferric ions. If it is assumed that all of the H_2O and $(\text{OH})^-$ groups are replaced, an essentially anhydrous spinel-type compound of $\text{ZnO-Fe}_2\text{O}_3$ could result according to the following scheme:

In this scheme the ZnO is postulated as reacting as a tetrahedral $\text{Zn}(\text{OH})_4^-$, which is said to exist⁽¹⁰⁾ in a form analogous to $\text{Si}(\text{OH})_4$. Scholder⁽¹¹⁻¹⁷⁾ and Emeleus⁽¹⁸⁾ have demonstrated the existence of salts such as $[\text{Zn}(\text{OH})_4] \text{Na}_2 \cdot 2\text{H}_2\text{O}$.

The above formulation, with all of the coordinated water on the iron complex, is shown although in all probability it does not exist. The compounds probably would be dehydrated spinels such as $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$. The net effect would be the elimination of $(\text{OH})^-$ from the adherent film and thus Fe^{++} or Fe^{+++} would not be attracted to the surface. The surface would tend to be "chemically polarized" and the progress of the oxidation should stop. Verwey⁽¹⁹⁾ observed that Fe_3O_4 , the normal magnetite corrosion product, is a fairly good electronic conductor with a resistivity of 5×10^{-3} ohm-cm; with increasing zinc content, the resistivity increases enormously. The full explanation depends upon the interchangeable occupancy of tetrahedral sites in the lattice of Fe_3O_4 by Fe^{++} or Fe^{+++} which can exchange electrons readily. If these sites are occupied by Zn^{++} , no such exchange is possible and a high-resistivity oxide is obtained. Therefore, in the case of an oxide film, zinc ions, if reacted, should stop the flow of electrons and help to prevent flow of electrons from the anode (metal) to the cathode (outer surface of oxide layer).

We have previously considered cases where the ferrous ions first formed are transformed into ferric ions, or, more correctly, into one of the insoluble ferric hydrous oxides such as $\text{FeO}(\text{OH})$. However, Schickorr^(20, 21) maintained that iron can corrode directly to

Fe₃O₄ by reaction with water. This was confirmed experimentally by Corey and Finnegan, (22) who found that iron powder is converted to Fe₃O₄ in oxygen-free water at 25C. Warner (23) showed on thermodynamic grounds also that such an oxidation is possible.

If this mechanism is correct, one would expect little effect from zinc as an inhibitor on mild steels since any oxygen present would probably be used to oxidize ferrous ions that had already gone into solution and thus be used up. Hence, a self-healing film would not be formed, since any further ferrous ions formed would form a fairly porous conducting Fe₃O₄ which would not be very protective. Alternatively, there may be so little ionic (hydrated) species of ferrous ions present at any given time that the zinc never has a chance of effectively reacting.

Since this type of work has not been done before at the temperatures used here, the mechanisms must be considered as merely types and the practical success obtained in these experiments should serve to motivate more detailed experimental work in deciding which mechanisms prevail.

III. EXPERIMENTAL EQUIPMENT AND PROCEDURE

A. Equipment

1. Autoclaves

The majority of the tests were performed in stainless steel (Type 304 or Type 347) autoclaves of about 100-ml capacity. In some cases autoclaves of larger capacity, but of similar design, were used. The volume of the test solution was usually 60-65% of the autoclave capacity.

The essential features of the autoclave are shown in Fig. 2.

Fig. 2
Autoclave Components

The sample holders were designed to hold the test specimens in an upright position, with a minimum area of contact between adjacent sample surfaces. Holes were punched in the horizontal disks to permit free convection of the test solution.

The autoclaves were heated in constant-temperature ovens designed to hold from 18 to 24 small autoclaves.

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2. Sample Preparation

The Type 347 samples were sawed, annealed, and machined on a shaper to about 15 micro-inch finish. In some cases, a shell cutter was used. The 2S aluminum samples were similarly machined. The SAE-1020 steel specimens were in the form of cylinders. The dimensions of the respective material specimens were as follows:

Type 347	2 x 3/8 x 3/16 in.
2S aluminum	1-1/2 x 3/4 x 1/16 in.
SAE-1020 steel	3/8 OD x 3/4 in.

All of the Type 347 samples were degreased in trichloroethylene and then pickled in a cold, 4% (by volume) HF-40% HNO₃ mixture for about 40 min. Aluminum samples were pickled only until a fairly vigorous reaction was observed. The samples were washed in deionized water and acetone, and air dried.

The SAE-1020 samples were stored in oil; just prior to test, they were degreased and dried.

The sample holders and the autoclaves were pickled in HF-HNO₃ solution.

B. Procedure

Each group of samples was weighed, mounted in the holder, and then inserted in respective autoclaves containing solutions of known conductivity and pH value.

The test solution was laboratory distilled and deionized water containing either laboratory-grade or commercial-grade chemical reagents. No special precautions were exercised to exclude soluble gases. A condition of oxygen saturation was used because it is easily reproduced. Oxygenation was accomplished by bubbling gas into the test solution immediately before inserting the samples and sealing the autoclave. A condition of hydrogen saturation was used with some inhibitors where there was a possibility of enhanced protection from the combination. In some cases, the SAE-1020 samples were immersed in a solution which was air-saturated at room temperature.

The autoclaves were sealed and heated to temperature in the oven for 1-week periods. Upon completion of the test period, the samples were removed, washed with water and acetone, air dried, and weighed. The changes in pH and conductivity, and the appearance of the solutions were noted.

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Since the evaluations were based on groups of solutions of different concentrations, no attempt was made to determine the amount of material used or to calculate the total metal surface to inhibitor weight.

IV. METHOD OF ANALYSIS AND RESULTS

Owing to the large number of solutions to be evaluated, coupled with a limited supply of available small autoclaves, each sample holder was designed to accommodate four specimens of rather small surface area. Hence, with samples as generally corrosion resistant as stainless steel, any gains in weight (which has never been a very reliable index of corrosion) become insignificant with respect to the corrosion behavior of the respective samples. It must be remembered that, in the early stages of the corrosion process, some of the oxide sloughs off or dissolves; subsequently it is competitive with gains in weight.

In the case of stainless steel, as the coating thickens it passes through several orders of interference colors, becomes dull, and finally black.

In the case of aluminum, the oxides generally thicken to the point of appearing crystalline at low-power magnification. This is followed by the appearance of "craters" of material which seem to contain metal, oxide, and moisture. Often, pitting is observed in the form of deep threads. Aluminum is very prone to pit or crater; hence, the effectiveness of an inhibitor is not always a function of gain in weight. A relatively large gain in weight may be the result of uniform oxide formation with freedom from pits. Under the best conditions only a thin diffraction oxide may form.

In the case of SAE-1020 steel, a smooth, rust-free surface is the criterion. It is uncommon to find an inhibitor which, at elevated temperatures, forms a diffraction oxide on SAE-1020 steel.

The more nearly a sample retains its original color and metallic reflectivity, the thinner is the oxide coating; therefore, the appearance of the samples was adjudged the primary index of inhibitor effectiveness.

A. Influence of Inhibitors on Corrosion of Type 347 Stainless Steel

1. Zinc Hydroxide

Samples exposed for 160 hr in oxygen-saturated solutions containing 50 to 500 ppm zinc oxide evidenced very little oxidation. All specimens were coated with a thin, transparent oxide, the color of which ranged from a shiny, light straw to a dark purplish hue (Table I).

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TABLE I

EFFECT OF ZINC HYDROXIDE ON CORROSION OF TYPE 347 STAINLESS STEEL
EXPOSED FOR 160 HOURS IN OXYGEN-SATURATED SOLUTION

ZnO CONC., ppm	WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
500	+0.01		SHINY, LIGHT STRAW; SOME END EFFECT
500	+0.03		SHINY, LIGHT STRAW; SOME END EFFECT
250	0.00		SHINY, MEDIUM STRAW; VERY SLIGHT END EFFECT
250	-0.02		SHINY, MEDIUM STRAW; VERY SLIGHT END EFFECT
100	-0.02		MEDIUM STRAW; SOME END EFFECT
100	-0.01		SHINY, DARK STRAW; STRONG END EFFECT
50	+0.06		LIGHT BLUE TO DARK STRAW; SOME END EFFECT
50	+0.01		SHINY LIGHT STRAW TO PURPLISH; SOME END EFFECT

Reproducibility of experimental results was demonstrated satisfactorily by a second group of samples exposed for 167 hr in respective solutions containing from 50 to 1000 ppm zinc oxide. These tests also served to provide "preconditioned" samples for subsequent evaluation studies.

Table II shows the results of a parallel test of the inhibitive properties of zinc hydroxide over a period of 741 hr. The appearance of the

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samples and the weight changes were substantially the same as observed on specimens exposed for one week. The test solutions showed either a white or reddish turbidity or a slightly black precipitate, indicative of some initial corrosion.

TABLE II
EFFECT OF ZINC HYDROXIDE ON CORROSION OF TYPE 347 STAINLESS STEEL
EXPOSED FOR 741 HOURS IN OXYGEN-SATURATED SOLUTION

ZnO CONC., ppm	WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
1000	-0.01		SHINY, DARK STRAW
1000	-0.01		SHINY, DARK STRAW; VERY LITTLE END EFFECT
500	+0.03		VERY LIGHT STRAW; ALMOST METALLIC
500	+0.03		VERY LIGHT STRAW; ALMOST METALLIC
250	-0.01		PURPLISH-STRAW; END EFFECT
250	+0.03		PURPLISH-STRAW; END EFFECT
100	+0.03		DARK STRAW TO PURPLE
100	+0.03		DARK STRAW TO PURPLE
50	+0.02		SHINY, TRANSPARENT, LIGHT BLUE TO STRAW
50	+0.01		PURPLE AND STRAW

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Tests were also made to determine the minimum zinc oxide concentration necessary to maintain a protective coating on a previously formed film. Samples representative of each "preconditioning" solution were exposed for one week in fresh solutions containing 50 and 10 ppm zinc oxide, respectively. There was no significant change in appearance of the samples and the solutions contained much less suspended material. The weight changes are given in Table III.

Table III

Influence of Zinc Hydroxide on Subsequent Corrosion
of Preconditioned Type 347 Stainless Steel Exposed
for One Week in Oxygen-Saturated Solutions

Preconditioning (167 hr)		Subsequent Test (160 hr)	
ZnO Conc., ppm	Wt. Change, mg/cm ²	ZnO Conc., ppm	Wt. Change, mg/cm ²
1000	0.00	50	+ 0.05
500	+ 0.01	50	+ 0.05
100	+ 0.01	50	+ 0.03
50	- 0.02	50	+ 0.05
1000	- 0.03	10	+ 0.06
500	0.00	10	+ 0.04
100	+ 0.01	10	+ 0.05
50	+ 0.02	10	+ 0.04

The samples were returned to test in the same solutions for a period of 329 hr. No changes in appearance were observed; weight changes ranged from 0.00 to 0.07 mg/cm².

For purposes of comparison, Table IV shows the progressive corrosion of Type 347 in an oxygenated solution with no reagent addition.

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TABLE IV
PROGRESSIVE CORROSION OF TYPE 347 IN OXYGEN-SATURATED
SOLUTION WITHOUT ZINC HYDROXIDE ADDITION

WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
	<u>TIME: 192 hr</u>	
+0.04		SHINY TO RATHER DULL LIGHT BROWN TO VERY DARK STRAW
+0.07		SHINY TO RATHER DULL LIGHT BROWN TO VERY DARK STRAW
+0.07		GREENISH TO DARK BROWN; TRANSPARENT TO DULL AT ENDS
+0.07		GREENISH TO DARK BROWN; TRANSPARENT TO DULL AT ENDS
	<u>TIME: 331 hr</u>	
+0.09		UNIFORM, DULL GRAY; NO END EFFECTS
+0.06		UNIFORM, DULL GRAY; NO END EFFECTS
+0.06		UNIFORM, DULL GRAY; NO END EFFECTS
+0.09		UNIFORM, DULL GRAY; NO END EFFECTS

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Table V shows the effect of a hydrogen-saturated solution containing zinc hydroxide on the corrosion of Type 347.

TABLE V
EFFECT OF ZINC HYDROXIDE ON CORROSION OF TYPE 347 EXPOSED FOR
168 HOURS IN HYDROGEN-SATURATED SOLUTIONS

ZnO CONC., ppm	WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
100	+0.03		SHINY, GOLDEN TO PURPLISH; NO END EFFECTS
100	+0.03		NO CHANGE IN APPEARANCE

2. Kadox

Kadox,* a very finely divided form of zinc oxide, was dispersed in ammonia and water. The ammonia was evaporated and the remaining slurry was used as an inhibitor. The oxide is the stable form in solutions at elevated temperatures.

Samples exposed for 162 hr in respective solutions containing 1000 ppm to 100 ppm zinc oxide showed a pronounced improvement in appearance (Table VI) over that exhibited by specimens exposed in the zinc hydroxide tests. In view of the sharp contrast of the sample at 50 ppm concentration, it may be assumed that some contaminant, e.g., chloride ion, absorbed by the ammonia dispersant from air was responsible for the very poor surface appearance. Subsequently, it was learned that dispersion with ammonia is not necessary.

*New Jersey Zinc Sales Co., New York, N. Y.

2a

TABLE VI
EFFECT OF KADOX ON CORROSION OF TYPE 347 STAINLESS STEEL
EXPOSED FOR 162 HOURS IN DEGASSED SOLUTIONS

ZnO CONC., ppm	WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
1000	0.00		SHINY, UNIFORM, MEDIUM STRAW
1000	+0.01		SHINY, UNIFORM, MEDIUM STRAW
500	0.00		SIMILAR IN APPEARANCE; END EFFECT
500	+0.01		SIMILAR IN APPEARANCE; END EFFECT
250	0.00		SHINY, GOLDEN TO DARK STRAW; SLIGHT END EFFECT
250	0.00		SHINY, GOLDEN TO DARK STRAW; SLIGHT END EFFECT
100	+0.01		LIGHT STRAW; SLIGHT END EFFECT
50	+0.01		DULL BLACK; VERY POOR

3. Zinc Metal

The use of metallic zinc as an inhibitor was premised on the theory that dissolution of the metal by corrosion would produce a very finely divided oxide; hence, zinc ion should be readily available to form a surface oxide. Also, as demonstrated by Taylor,⁽²⁴⁾ zinc oxide has some catalytic effect on hydrogen formation of monatomic or free radical hydrogen; thus the evolved hydrogen could serve as an interim inhibitor until the zinc oxide concentration was sufficient to form a protective film on the stainless steel.

Table VII shows the contrast in surface appearance effected by the respective test environments. While the weight gains of the blank samples (no additive) are somewhat higher than their counterparts in the zinc-containing solutions, the significant difference is illustrated by the dull appearance of the blank samples. The initial atmosphere of hydrogen showed no inhibitive effect on the appearance of the blank samples, as contrasted to the specimen in the oxygen-saturated, 500-ppm solution.

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TABLE VII

EFFECT OF METALLIC ZINC ON CORROSION OF TYPE 347
STAINLESS STEEL EXPOSED 162 HOURS IN RESPECTIVE
DEGASSED, OXYGENATED, AND HYDROGENATED SOLUTIONS

ZnO CONC., ppm	WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
500*	+0.02		METALLIC TO LIGHT STRAW; NO END EFFECT
500	+0.03		METALLIC TO LIGHT STRAW; NO END EFFECT
250	+0.05		VERY LIGHT STRAW; SOME END EFFECT
250	+0.03		VERY LIGHT STRAW; SOME END EFFECT
100	+0.03		VERY LIGHT STRAW; SOME END EFFECT
100	+0.06		VERY LIGHT STRAW; SOME END EFFECT
50	+0.06		VERY LIGHT STRAW; SOME END EFFECT
0**	+0.05		DULL, DARK PURPLE
0**	+0.07		DULL, DARK PURPLE
0*	+0.09		DULL, DARK PURPLE; BRONZE, ALMOST BLACK

* OXYGEN SATURATED

** HYDROGEN SATURATED

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The absence of brownish turbidity in the test solutions, and the appearance of the samples affirm the effectiveness of zinc metal as corrosion inhibitor for Type 347.

4. Zinc Nitrate

Since zinc nitrate would be in a highly ionized state, the zinc ion should be readily available for forming an oxide layer. Further, a slight etching of the metal surface by the nitrate ion might prove beneficial in providing direct access of the zinc ions to the bare metal, thereby accelerating the formation of a stabilized oxide layer.

The etching action was confirmed by the weight losses registered by all samples (Table VIII). Each test solution showed a yellow turbidity, indicating the presence of ferric ions.

TABLE VIII
EFFECT OF ZINC NITRATE ON CORROSION OF TYPE 347 STAINLESS STEEL
EXPOSED FOR 162 HOURS IN DEGASSED SOLUTIONS

<u>ZnO CONC., ppm</u>	<u>WT. CHANGE, mg/cm²</u>	<u>SURFACE APPEARANCE</u>
800	-0.01	METALLIC, WITH DEPOSITED HAZE
800	-0.03	METALLIC, WITH DEPOSITED HAZE
500	-0.09	VERY LIGHT STRAW; SLIGHT HAZE
500	-0.12	VERY LIGHT STRAW; SLIGHT HAZE
100	-0.08	FAINT STRAW; ALMOST METALLIC; SLIGHT HAZE; SLIGHT END EFFECT
100	-0.06	FAINT STRAW; ALMOST METALLIC; SLIGHT HAZE; SLIGHT END EFFECT
50	-0.08	VERY LIGHT STRAW
10	-0.07	BROWNISH-BLUI SH BRONZE

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5. Zinc Acetate

The excellent effect of zinc nitrate in forming thin oxide layers on stainless steel prompted tests to observe the inhibiting properties of the more weakly ionized acetate.

The samples registered some gains in weight; all were coated with a very light oxide film (Table IX). The test solutions showed slight turbidity.

TABLE IX
EFFECT OF ZINC ACETATE ON CORROSION OF TYPE 347 STAINLESS STEEL
EXPOSED FOR 165 HOURS IN OXYGEN-SATURATED SOLUTIONS

ZnO CONC., ppm	WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
1000	+0.03		VERY LIGHT STRAW; ALMOST ORIGINAL CONDITION; SLIGHT END EFFECT
1000	+0.03		SIMILAR IN APPEARANCE
500	+0.04		SIMILAR IN APPEARANCE
500	+0.03		SIMILAR IN APPEARANCE
250	+0.05		SLIGHTLY DARKER STRAW; SOME END EFFECT
250	+0.05		SIMILAR IN APPEARANCE
100	+0.06		LIGHT STRAW; VERY SLIGHT END EFFECT
50	+0.04		VERY LIGHT STRAW

24 6. Zinc Oxide - Zinc Acetate Mixture

Samples were exposed for three successive weekly periods in a solution containing a mixture of zinc oxide (Kadox) and zinc acetate. The ratio of zinc oxide, as such, to zinc oxide as the acetate was 1:0.255. The test solution, containing 125 ppm (equivalent) ZnO, was saturated with oxygen at the start of the test and at the start of each subsequent test period.

All samples retained a light straw, almost original metallic color throughout the duration of the test (Table X). Moderate weight gains were registered during the first two weeks, with a slight loss in weight during the third week.

TABLE X
EFFECT OF ZINC OXIDE-ZINC ACETATE MIXTURE ON CORROSION OF TYPE 347 STAINLESS STEEL EXPOSED FOR 492 HOURS IN OXYGEN-SATURATED SOLUTION

ZnO CONC., ppm	WT. CHANGE, mg/cm ²		SURFACE APPEARANCE
			<u>TEST PERIOD: 161 hr</u>
125	+0.05		LIGHT STRAW; METALLIC
125	+0.04		SIMILAR IN APPEARANCE; TWO SLIGHTLY DULL SPOTS
			<u>TEST PERIOD: 166 hr</u>
125	+0.02	}	NO CHANGE IN APPEARANCE
125	+0.03		
			<u>TEST PERIOD: 165 hr</u>
125	-0.01	}	NO CHANGE IN APPEARANCE
125	-0.02		

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7. Zinc Silicofluoride

Zinc silicofluoride was used as a further test of the effectiveness of zinc ion as an inhibitor in the presence of anions. However, since the fluoride may be expected to cause some corrosion, the maximum amount of salt used was 100 ppm, corresponding to 25 ppm zinc oxide.

All samples exhibited satisfactory surface appearance and weight changes after 161 hr exposure to oxygen-saturated solutions containing from 25 ppm to 1.3 ppm zinc oxide (Table XI).

TABLE XI
EFFECT OF ZINC SILICOFLUORIDE ON CORROSION OF TYPE 347 STAINLESS STEEL
EXPOSED FOR 161 HOURS IN OXYGEN-SATURATED SOLUTIONS

CONCENTRATION, ppm		WT. CHANGE, mg/cm ²		SURFACE APPEARANCE
ZnSiF ₆	EQUIV. ZnO			
100	25	+0.01		LIGHT METALLIC; SOME OPACITY AT ONE EDGE
50	12.5	+0.01		LIGHT METALLIC; SOME OPACITY AT ONE EDGE
50	12.5	+0.03		LIGHT METALLIC; SOME OPACITY AT ONE EDGE
20	5.1	+0.03		LIGHT STRAW; DARK SPOTS; SHINY, TRANSPARENT OXIDE
20	5.1	+0.03		STRAW; SLIGHTLY SPOTTED
10	2.6	+0.04		DARK STRAW TO BROWN; SLIGHTLY SPOTTED
10	2.6	+0.03		STRAW TO DARK BROWN; UNEVEN FILM
5	1.3	+0.03		LIGHT TO DARK STRAW
5	1.3	0.00		LIGHT TO DARK STRAW

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B. Influence of Inhibitors on Corrosion of 2S Aluminum

Zinc oxide was evaluated as an inhibitor for 2S aluminum even though zinc is usually cathodic to aluminum.

1. Zinc Hydroxide; Zinc Carbonate; Zinc Acetate

Table XII is a composite of samples exposed for 165 hr in respective oxygen-saturated solutions containing 250 ppm and 50 ppm of zinc hydroxide, zinc carbonate, and zinc acetate.

TABLE XII
EFFECT OF VARIOUS IONIC FORMS OF ZINC ON CORROSION OF
2S ALUMINUM EXPOSED 165 HOURS IN OXYGEN-SATURATED SOLUTIONS

ZnO CONC., ppm	WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
ZINC HYDROXIDE			
250	+0.01		SMOOTH; SLIGHTLY ETCHED CRYSTALLINE; GRAY OXIDE
50	+3.14		ETCHED CRYSTALLINE OXIDE ALL OVER
ZINC CARBONATE			
250	+1.99		SMOOTH ETCHED SURFACE; SLIGHTLY CRYSTALLINE
50	+1.91		SIMILAR IN APPEARANCE
ZINC ACETATE			
250	+0.63		ALMOST METALLIC; MICROSCOPIC ETCH
50	+0.84		UNIFORM, SMOOTH, GRAY OXIDE CRYSTALLINE

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That the zinc oxide afforded some protection is best illustrated by the progressively poorer appearance of similar specimens as a function of continued exposure to water without reagent addition (Fig. 3).

NOTE: PARENTHEZIZED NUMBERS ARE WEIGHT CHANGES IN mg/cm²

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FIG 3
PROGRESSIVE CORROSION OF 2S ALUMINUM IN 500 F DEGASSED WATER

2. Zinc Oxide - Zinc Acetate Mixture

As in the case of Type 347, samples of 2S aluminum were exposed for three successive weekly periods in respective solutions containing various concentrations of a zinc oxide-zinc acetate mixture [1 part zinc oxide (Kadox) to 0.25 part zinc oxide as the acetate]. Each solution was saturated with oxygen at the start of the first test period.

A comparison of the results (Table XIII) with Table XII shows that the mixture is not as effective as the acetate alone. However, there was a sharp concentration dependence; the samples at higher concentrations exhibited the least gains in weight.

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TABLE XIII

EFFECT OF ZINC OXIDE-ZINC ACETATE MIXTURE ON CORROSION OF
2S ALUMINUM EXPOSED FOR 492 HOURS IN OXYGEN-SATURATED SOLUTIONS

ZnO CONC., ppm	WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
<u>TEST PERIOD: 161 hr</u>			
1250	+0.39		LIGHT-COLORED, THIN OXIDE COATING; NUMEROUS SMALL PITS
625	+1.77		LIGHT-COLORED CRYSTALLINE OXIDE COATING
250	+1.84		GRAY CRYSTALLINE OXIDE COATING; ETCHED EFFECT NEAR CENTER
125	+1.93		SIMILAR IN APPEARANCE; PITTING NEAR EDGES
50	+1.88		SIMILAR IN APPEARANCE; STARTING TO PIT
<u>TEST PERIOD: 165 hr</u>			
1250	+0.68	METALLIC; PATCHY LOCALIZED ATTACK	
625	+0.64	METALLIC NEAR ENDS; WHITE, FLAKEY OXIDE NEAR CENTER; PITTING	
250	+1.21	GRAY, ETCHED, VERY SLIGHT DIFFUSED LOCALIZED ATTACK	
125	+1.04	SAME CRYSTALLINE OXIDE; SLIGHT LOCALIZED ATTACK AT EDGES	
50	+2.45	LOCALIZED ATTACK AT EDGES	
<u>TEST PERIOD: 166 hr</u>			
625	+0.38	HEAVY CRYSTALLINE OXIDE COATING	
250	+3.24	HEAVY CRYSTALLINE OXIDE COATING	
125	+2.57	HEAVY CRYSTALLINE OXIDE COATING	

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3. Zinc Nitrate; Zinc Silicofluoride

As evidenced by Tables XIV and XV, both the nitrate and the silicofluoride ions proved detrimental to aluminum in the presence of zinc.

TABLE XIV

EFFECT OF ZINC NITRATE ON CORROSION OF 2S ALUMINUM
EXPOSED FOR 162 HOURS IN OXYGEN-SATURATED SOLUTIONS

ZnO CONC., ppm	WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
800	+2.24		PATCHY, DARK CRYSTALLINE OXIDE; PITS STARTING
500	+1.50		BUMPY, CRYSTALLINE OXIDE; SMALL PITS
100	+3.41		SIMILAR IN APPEARANCE
50	+3.32		CRYSTALLINE OXIDE; PITS STARTING
10	+2.33		ETCHED, BUMPY CRYSTALLINE OXIDE; LIGHT GRAY

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TABLE XV

EFFECT OF ZINC SILICOFLUORIDE ON CORROSION OF 2S ALUMINUM
EXPOSED FOR 161 HOURS IN DEGASSED SOLUTIONS

ZnO CONC., ppm	WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
100	+8.0		DARK GRAY; MICROSCOPIC ETCHED, BUMPY CRYSTALLINE OXIDE
50	+7.0		SIMILAR IN APPEARANCE
20	+5.12		DARK GRAY; BUMPY CRYSTALLINE OXIDE
10	+4.14		GRAY; ETCHED, BUMPY CRYSTALLINE OXIDE
5	+4.49		ETCHED, BUMPY; CRYSTALLINE UNDER MICROSCOPE

C. Influence of Zinc Hydroxide on Corrosion of SAE-1020 Steel

Cylindrical samples of SAE-1020 steel were exposed for one week in respective oxygenated and hydrogenated solutions containing from 1000 to 250 ppm zinc oxide.

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While all samples experienced a weight loss, the lesser weight losses were registered by specimens in the hydrogenated solutions (Table XVI). However, the weight losses in both instances exceed the losses suffered by specimens exposed in similar environments, without reagent additives (Table XVII).

Table XVI

Effect of Zinc Hydroxide on Corrosion of SAE-1020 Steel
Exposed for 161 Hours in Respective Oxygenated and
Hydrogenated Solutions

ZnO Conc., ppm	Wt. Change, mg/cm ²	
	Oxygenated	Hydrogenated
1000	-1.60	-1.10
1000	-1.00	-0.90
500	-1.30	-0.50
500	-1.20	-0.50
250	-1.40	-1.00
250	-1.30	-0.90

TABLE XVII

CORROSION OF SAE-1020 STEEL IN OXYGENATED
AND HYDROGENATED WATER WITHOUT REAGENT ADDITION

WT. CHANGE, mg/cm ²	SURFACE APPEARANCE	
	OXYGENATED	
-1.04		BLACK MAGNETIC COATING; SLIGHT PITTING
-1.02		SIMILAR IN APPEARANCE
	HYDROGENATED
	BLACK MAGNETITE, BUT MUCH SMOOTHER
-0.79		SIMILAR IN APPEARANCE

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The samples were returned to test for an additional 162 hr in freshly prepared solutions. The weight losses for this period (Table XVIII) were approximately one-half the values registered during the initial test period.

Table XVIII

Subsequent Corrosion of SAE-1020 Samples Exposed
for 162 Hours in Fresh Solutions

ZnO Conc., ppm	Wt. Change, mg/cm ²	
	Oxygenated	Hydrogenated
1000	-0.52	-0.30
1000	-0.50	-0.50
500	-0.10	-0.50
500	-0.20	-0.30
250	-0.60	-0.50
250	-0.50	-0.50

The blank samples were not returned for additional test; hence it is uncertain whether the significant decrease in weight loss was due to protection by the magnetite or to inhibition by the zinc oxide.

V. SUMMARY

Sources of zinc ion - zinc hydroxide, acetate, nitrate, silicofluoride, and zinc metal - are particularly effective corrosion inhibitors for Type 347 stainless steel for periods up to 740 hours in static, oxygenated water at 500F. Concentrations of 50 ppm and 500 ppm equivalent zinc oxide are equally effective. Inhibition is enhanced slightly in hydrogenated water, as evidenced by elimination of concentration cell or end effects.

Zinc oxide in the form of a commercial pigment (Kadox) is fully effective as reagent grade zinc hydroxide.

Samples exposed in solutions containing zinc acetate exhibit a thinner and more protective coating. A mixture of the acetate with Kadox is more effective than the oxide alone.

The nitrate and silicofluoride are most promising as preconditioners. The nitrate ion is somewhat corrosive to Type 347 even though it does form an excellent film.

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Solutions containing as low as 10 ppm equivalent zinc oxide are sufficient to maintain previously formed protective films for periods up to 660 hours.

Zinc acetate at concentrations of 250 and 50 ppm is predominantly effective as an inhibitor for 2S aluminum. The nitrate and the silicofluoride are more detrimental than protective.

The limited number of tests precludes a comparison of the relative merits of the various zinc oxides as inhibitors for SAE-1020 steel. The excessive weight losses in oxygenated and in hydrogenated solutions attest to the ineffectiveness of zinc hydroxide. In both instances, the weight losses exceed those exhibited by specimens exposed concurrently in untreated, degassed water. On the other hand the magnetite layers observed on the latter specimens may have served to retard accelerated corrosion attack.

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BIBLIOGRAPHY

1. C. Wohlberg and F. W. Kleimola, "Factors Which Affect Formation and Deposition of Transport Corrosion Products in High-Temperature Recirculating Water Loops," ANL-5195 (December, 1953).
2. N. Cabrera and N. F. Mott, "Theory of the Oxidation of Metals" in Physical Society of London, "Reports on Progress in Physics," V. 12, 163-184 (1948-49).
3. L. B. Pfeil, "The Oxidation of Iron and Steel at High Temperatures" Journal of Iron and Steel Institute, 119 No. 1, 501-560 (1929).
4. H. H. Uhlig, "The Corrosion Handbook," (New York: John Wiley & Sons, Inc., 1948).
5. W. J. Parker, Journal of Iron and Steel Institute (England), 1881, p. 39.
6. U. R. Evans, "The Action of Salt Solutions on Iron and Steel and the Presence of Oxygen" Journal of the Society of Chemical Industry Transactions, 43, 315T (1924).
7. R. S. Thornhill, "Zinc, Manganese, and Chromic Salts as Corrosion Inhibitors" Ind. and Eng. Chem., 37, 706-708 (1945).
8. B. L. Cross and N. Hackerman, "Corrosion," 10, 407 (1954).
9. U. R. Evans, "Use of Soluble Inhibitors" Industrial and Engineering Chemistry, 37, 703-706, 1945.
10. W. Huckel, "Structural Chemistry of Inorganic Compounds," (Elsevier Publishing Co., 1950) Vol. II, p. 882.
11. Von R. Scholder und G. Hendrich, Das system $\text{AnO-Na}_2\text{O-H}_2\text{O}$. Z. anorg. u. allgem. Chem. 241, 76-92 (1939).
12. Von R. Scholder und H. Weber, Das amphotere Verhalten von Metallhydroxyden II. Uber Zinkate. Z. anorg. u. allgem. Chem., 215, 355-68 (1933).
13. Von R. Scholder, R. Felsenstein und A. Apel, Das amphotere Verhalten von Metallhydroxyden III. Uber Cuprite. Z. anorg. u. allgem. Chem., 216, 138-44 (1933).
14. Von R. Scholder und H. Weber, Das amphotere Verhalten von Metallhydroxyden IV. Uber Koballite. Z. anorg. u. allgem. Chem., 216, 159-64 (1933).

15. Von R. Scholder und R. Patsch, Das amphotere Verhalten von Metallhydroxyden V. Über Stannite. Z. anorg. u. allgem. Chem., 216, 176-84 (1933).
16. Von R. Scholder und R. Patsch, Das amphotere Verhalten von Metallhydroxyden VI Über Plumbite. Z. anorg. u. allgem. Chem., 217, 214-24 (1933).
17. Von R. Scholder und R. Patsch, Das amphotere Verhalten von Metallhydroxyden VIII Über Chromite. Z. anorg. u. allgem. Chem., 220, 411-24 (1934).
18. H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," (London: Routledge and Kegan Paul Ltd.) p. 199.
19. E. J. Verwey, "Atomic Arrangement in Spinel in Connection with their Physical Properties" Proc. 11th International Congress of Pure and Applied Chemistry, 1, 285-291 (1947).
20. Von Gerhard Schikorr, Über Eisen (II)-hydroxyd und ein ferromagnetisches Eisen (III)-hydroxyd. Z. anorg. u. allgem. Chem., 212, 33-9 (1933).
21. Von G. Schikorr, Über das system eisen-wasser. Z. Elektrochem., 35, 62-5 (1929).
22. Richard C. Corey and Thomas J. Finnegan, "The pH, Dissolved Iron Concentration and Solid Product Resulting from the Reaction Between Iron and Pure Water at Room Temperature," American Society for Testing Materials Proceedings 39, 1242-1253 (1939).
23. J. C. Warner, "Discussion on Reaction Between Iron and Pure Water," American Society for Testing Materials Proceedings 39, 1257-58 (1939).
24. G. M. Schwab, "Catalysis from the Standpoint of Chemical Kinetics," (New York: Van Nostrand Co., Inc., 1937). Translated from the First German Edition with additions from the recent literature by the author, by H. S. Taylor and R. Spence.

36ACKNOWLEDGEMENT

The author gratefully acknowledges the assistance rendered by his associates during the course of the investigation. Due credit is given to Messrs. Sherman Greenberg and Vincent Saitta who originally designed the test autoclaves; to Mr. C. Kuhnhofer who collaborated with Mr. Greenberg in the design of the autoclave gasket, a most essential feature of the test equipment; and to Mr. J. Brichta who performed most of the experimental work.