195
8-3

RFP-1868

2221

RFP-1868
July 7, 1972

MASTER

LITERATURE SURVEY OF CORROSION INHIBITORS
FOR RECIRCULATING COOLING WATER
CORROSION INHIBITION

John L. Briggs

DOW CHEMICAL U.S.A.
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

U. S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America
Available from the
National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

Printed Date
July 7, 1972

RFP-1868
UC-4 CHEMISTRY
TID-4500 - 56th Ed.

LITERATURE SURVEY OF CORROSION INHIBITORS
FOR RECIRCULATING COOLING WATER
CORROSION INHIBITION

John L. Briggs

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DOW CHEMICAL U.S.A.
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

Prepared under Contract AT(29-1)-1106
for the
Albuquerque Operations Office
U. S. Atomic Energy Commission

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

Abstract	1
Introduction	1
Cooling Water Systems at Rocky Flats	1
Metallic Corrosion	2
Inhibitor Classification	2
Inorganic Cathodic Inhibitors	2
Inorganic Anodic Inhibitors	2
Organic Inhibitors	2
Protective Film Theory	5
Adsorption Theory	5
Chromates	5
Phosphates	8
Nitrites	9
Silicates	10
Conclusions	12
References	12

LITERATURE SURVEY OF CORROSION INHIBITORS FOR RECIRCULATING COOLING WATER CORROSION INHIBITION

John L. Briggs

Abstract. A literature survey was conducted to provide information concerning the chemical treatment of cooling water. Special emphasis was on the inhibition of metallic corrosion in open, recirculating cooling water systems.

The mechanism, effectiveness, performance, and potential use of several commonly used anodic corrosion inhibitors are included in the report.

INTRODUCTION

The prevention of metallic corrosion in recirculating cooling water systems is a problem confronting most industries and has been a subject of extensive study for the past thirty years. The use of chemical inhibitors has progressed to the point that by judicious selection of inhibitor treatment, metallic corrosion may be effectively controlled in most recirculating cooling water systems.

The literature survey presented herein has been conducted to provide information concerning the chemical treatment of cooling water. Special emphasis is on the inhibition of metallic corrosion in recirculating cooling water systems.

The term "inhibitor" is defined as any substance which decreases the corrosion rate of a metal when added in small quantities to a corrosive environment.^{1,2} Although this survey is concerned primarily with the prevention of metallic corrosion, it is acknowledged that other problems are often interrelated with metallic corrosion.^{3,4} Information concerning these other problems is included in this report if the data are relevant to metallic corrosion inhibition. Proprietary inhibitor data are available for prospective water treatment programs; however, the information in this report was obtained from published literature.

COOLING WATER SYSTEMS AT ROCKY FLATS

A major portion of the water consumption at Rocky Flats is used for cooling water service. A high rate of cooling water use is typical of industries in the United States.⁵ Approximately seven million gallons of water per month are used at Rocky Flats for cooling purposes, and this is nearly half the total plant intake (15,735,000 gal/month).

Most of the cooling water is used by the open recirculating systems and consumed by evaporation at the cooling water towers. A small amount of cooling water is consumed during "bleed off," which is discharge followed by dilution of the recirculating water to reduce solids concentration.^{3,6} Bleed off is essential to ensure proper inhibitor concentrations for suitable water treatment. Closed recirculating systems require little or no make-up water; therefore monthly consumption of fresh water is negligible.

A typical analysis of the waters at Rocky Flats is shown in Table 1.⁷ Both potable and nonpotable waters are presently used for cooling purposes; however, a pipeline is being constructed which will supply untreated (nonpotable) water to all the major cooling towers on the plant site.

Table 1. Analysis of Rocky Flats Cooling Water (Semi-Annual Composite Samples, ppm).*

Constituent Sought (ppm)	Treated (potable) Water		Untreated (nonpotable) Water	
	Winter Composite 10/70-4/71	Summer Composite 4/71-10/71	Winter Composite 10/70-4/71	Summer Composite 4/71-10/71
Solids:				
Total	111	46	93	50
Dissolved	78	42	NA**	NA
Suspended	333	4	NA	NA
Loss on Ignition	20	28	NA	NA
Turbidity	0.68	1.5	NA	NA
Nitrogen As:				
Nitrates	0.05	0.03	0.07	0.08
Nitrites	0.04	<0.002		
Chloride	3.0	<1.0	0.40	<1.0
Hardness as CaCO ₃	55.5	19.6	43.4	26.7
Alkalinity:				
Bicarbonate, HCO ₃	64.6	36.7	56.4	44.4
Carbonate, CO ₃	None	None	None	None
Chromium, Cr ⁶⁺ (as Na ₂ CrO ₄)	<0.05	<0.05	<0.05	<0.05
Silica, SiO ₂	2.1	2.8	20.2	4.2
Sulfate, SO ₄	25.7	5.1	16.3	4.5
Calcium, Ca	17.5	6.7	13.2	8.9
Magnesium, Mg	4.3	1.1	3.3	1.6
Sodium, Na	10.4	6.6	7.3	5.8
Iron and Aluminum Oxides, Fe	3.5 (0.31)	3.0 (0.23)	9.5 (0.88)	5.0 (0.18)
Fluoride, F	0.13	0.13	<0.1	0.11
pH	8.1	8.1	7.6	7.6

*Analytical Laboratory Water Analysis Reports, April 5, 1971, and October 25, 1971, Rocky Flats Division, Dow Chemical U.S.A.

**NA = No analysis.

The very low mineral content of the soft (low hardness, low solids) water now being used at Rocky Flats reduces the problem of scaling or deposit formation. However, this soft water does increase the need for preventing metallic corrosion. Inhibition studies at Monsanto Chemical Company showed that soft water is the most corrosive water to steel and is also difficult to treat properly.⁸

Excluding the wooden cooling towers in the open recirculating systems, most of the water cooling equipment at Rocky Flats is steel; therefore, the prevention of metallic corrosion by means of suitable water treatment programs is essential.

METALLIC CORROSION

The corrosion of metals in water has been a problem since man first used metal. Early attempts by the Romans to prevent aqueous metal corrosion involved the use of protective coatings such as tar or bitumens.⁹ Protective coatings such as bitumen coatings for underground pipes and zinc coatings on galvanized steel are still used. The treatment of water with various chemical inhibitors to prevent corrosion has been practiced in recent times.

A reference list¹⁰ of cooling water inhibitors has been published by the National Association of Corrosion Engineers. The partial list shown in Table 2 includes only inhibitors for which literature references are available and does not include manufacturers' literature.

A wide variety of area and process conditions such as system water temperature, atmospheric contamination, and water velocity, must be considered when selecting the proper corrosion inhibitor for cooling water treatment.

Another consideration in the selection of suitable corrosion inhibitors for cooling water treatment is the numerous water impurities which can influence inhibitor performance. All natural and treated water may contain any of the following conditions: hardness, mineral acidity, turbidity, sediment, microbiological growths, silica, iron, manganese, carbon dioxide, oxygen, nitrogen, methane, sodium, and potassium salts.¹¹

INHIBITOR CLASSIFICATION

A system of classifying corrosion inhibitors is necessary because of the many types that are available to prospective users. Two main chemical classifications are organic and inorganic corrosion inhibitors. The inorganic inhibitors may be subclassified as cathodic or anodic according to the mechanism of inhibition.

INORGANIC CATHODIC INHIBITORS

Cathodic inhibitors are inhibitors that retard the cathodic reaction $O_2 + 2H_2O + 4e = 4(OH)$, whereas the mechanism of anodic inhibitors is unclear, it is generally agreed that cathodic inhibitors function by forming sparingly soluble hydroxides which resist oxygen and hydrogen hydrogen reduction at cathode areas.¹²⁻¹⁴

Typical cathodic inhibitors are the salts of zinc, chromium, manganese, and nickel.^{10,15} Cathodic inhibitors are considered "safe" in that low concentrations of cathodic inhibitors do not cause accelerated corrosion as do the "dangerous" anodic inorganic inhibitors.¹⁴

Thornhill, however, did observe intensified waterline corrosion with high concentrations of zinc and chromium cathodic inhibitors.¹⁴ Evans states that under the right conditions any type inhibition which forms a protective layer may cause accelerated corrosion.¹⁴ The literature indicates cathodic inhibitors are less widely used for recirculating cooling water systems, probably because of their ineffectiveness compared to anodic inhibitors.

INORGANIC ANODIC INHIBITORS

Anodic inhibitors are those chemical substances that retard or arrest anodic reactions (e.g., $Fe = Fe^{++} + 2e$).¹²

Anodic inhibitors have been described as "dangerous" inhibitors owing to the accelerated corrosion resulting when insufficient inhibitor concentration is present.^{14,21}

The anodic inhibitors have been widely studied and considerable controversy exists concerning the mechanism of anodic inhibition.^{9,13}

ORGANIC INHIBITORS

Although it is agreed that organic inhibitors function by adsorbing on metal surfaces, there is some question as to how the adsorbed organic molecule inhibits corrosion.¹⁶

One theory states that organic inhibitors which contain more than one functional group, function by chelating the nonsolubilized metal ion while the ion is still associated with its crystal lattice. The surface chelate then functions as a barrier which inhibits corrosion.¹⁷

Another generally accepted mechanism for organic inhibition is that initial physical adsorption of the inhibitor molecule is followed by a chemisorption process resulting in a protective film of chemical inhibition.^{10,16,17}

Table 2. Reference List of Cooling Water Inhibitors

Chemical Names	Trade Names	Effective With	References
Calcium Hydroxide		Fe, Zn, Cu, Brass	Corrosion Causes & Prevention, 2nd Edition, 361-366
Chromates		Fe, Zn, Cu, Brass	Ind. & Engr. Chem. Vol. 41, No. 11, 2376-2382 (1949); Oil & Gas J., Vol. 47, No. 37, 83-87 (1949) Jan 13.
Molecularly Dehydrated Phosphates and Chromates	Orocol	Fe, Zn, Cu, Brass	Oil & Gas J., Vol. 49, No. 43, 52-62 (1951) March 1; Ind. & Engr. Chem., Vol. 44, No. 8, 1770-1774 (1952); Corrosion, Vol. 6, No. 10, 331-340 (1947) Oct.
Molecularly Dehydrated Phosphates and Ferro Cyanides	Nalco No. 33	Fe, Zn, Cu	Oil & Gas J., Vol. 49, No. 43, 52-62 (1951) March 1.
Molecularly Dehydrated Phosphates and Organics	Phosphoglucosate	Fe, Zn, Cu, Brass	Oil & Gas J., Vol 49, No. 43, 52-62 (1951) March 1; Ind. & Engr. Chem., Vol 30, No. 12 1356-1361
Molecularly Dehydrated Phosphates and Silicates		Fe, Zn, Cu, Brass	Corrosion, Vol. 8, No. 12, 402-406 (1952) Dec.
Phosphates, Hexameta, Na & Ca	Micromet	Fe, Zn, Cu, Al, Brass	Ind. & Engr. Chem., Vol. 37, No. 8, 724-735 (1945) Aug.
Sodium Benzoate		Fe	Journal Soc. Chem. Indus. (Br.), Vol. 66, 137; Chem. & Ind. (Br.), Vol. 53, 1194 (1951).
Sodium Hexametaphosphate	Calgon	Fe, Zn, Cu, Pb, Brass	Corrosion, Vol. 8, No. 11, 381-390 (1952) Nov; Ind. & Engr. Chem., Vol. 32, No. 12, 1572-1579 (1938) Dec.
Sodium Hydroxide		Fe, Zn, Cu, Brass	Ind. & Engr. Chem., Vol. 37, No. 8, 724-735 (1945) Aug.
Sodium Nitrate		Fe, Zn, Cu, Al, Brass	Journal Electrochemical Soc., Vol. 93, 63 (1948); Ind. & Engr. Chem., Vol 35, 358 (1943).
Sodium Septa	Nalco No. 918	Fe, Zn, Cu, Al, Brass	Ind. & Engr. Chem., Vol 37, No. 8, 724-735 (1948) Aug.
Sodium Silicate		Fe, Zn, Cu, Brass	Ind. & Engr. Chem., Vol. 30, No. 3, 348-351 (1938) March; Ind. & Engr. Chem., Vol. 44, No. 8, 1765-1769 (1952) Aug.
Sodium Sulfite		All Metals	Petro. Processing, Vol. 7, No. 5, 620-622 (1952) May; J. Amer. Water Works Assoc., 39 (1121) (1947).
Tetraphosphoglucosate		Fe, Zn, Cu, Al, Brass	Ind. & Engr. Chem., Vol. 37, No. 8, 724-735 (1945) Aug.

Some use has been made of film forming and colloidal organic inhibitors such as alkali tannates, lignin, glucosate, starch, and acylation products of polyamines in cooling water towers where excessive contamination by carbon dioxide, dust, and bacteria exist.^{1,16,18}

Water cooling towers have also been treated with amino-methylene-phosphonate plus zinc, polyol-ester phosphate, and poly-acrylamide-silica polymers.³

Water soluble oil inhibitors have been effectively used in closed recirculating systems such as diesel and automobile radiators.^{19,20} However, their use in open industrial cooling water systems is not common because of their scum-forming tendency and lack of stability at elevated temperatures.²¹

Some other organic inhibitors that have been used in various applications for their protective effects in water are crude guinaldine, crude beet sugar, and natural glucosides.¹⁶

The desirable properties of organic inhibitors have been summarized by Breston as follows:¹⁶

1. Polarity is common in all organic inhibitors to prevent corrosion in aqueous media. They must be soluble or dispersible in water so that the metal to be protected may be wetted by the inhibitor.
2. The adsorbed layer on the metal to be protected should be uniform and not susceptible to excessive build-up.
3. Nontoxicity is essential in systems where waste water disposal restrictions exist.
4. The organic inhibitor must be physically and chemically stable.
5. The inhibitor should be effective at low concentrations.

Farnsworth has described the effective treatment of open cooling water systems with active blends of inhibitors. Exact molecular formulas were not given but the inhibitors were described as low to medium molecular weight anionic poly-electrolytes with zinc salts added. The addition of zinc permitted lower levels of inhibition concentration as shown in Table 3.²²

Table 3. Effect of Zinc Addition to Organic Inhibitors.*

Organic Mix (ppm)	Zn (ppm)	Corrosion Rate (mpy)
300	0	2.7
150	0	9.0
100	25	0.9
45	8	1.2
30	5	1.3

*N. B. Farnsworth and R. S. Robertson, "Non-Chromate Non-Phosphate Organic Cooling Water Treatments," *Materials Protection*, 5, No. 2, 15 (1966).

Tests were also conducted to compare the effectiveness of organic inhibitors with standard phosphate and chromate treatments. The results which are shown in Table 4 indicate the effectiveness of the organic inhibitor is comparable to the chromate and phosphate inhibitors.

Table 4. Comparative Performance of Organic Treatment with Standard Treatments on Steel.*

Inhibitor Treatment	CrO ₄ or PO ₄ Level (ppm)	Corrosion Rate (mpy)
Blank (7 days)	0	200.0
Synergized Chromate	10-20	1.2
Chromate with Organic	10-15	1.7
Synergized Phosphate	15-20	1.9
Phosphate with Organic	10	1.4
New Treatment	0	1.1

*N. B. Farnsworth and R. S. Robertson, "Non-Chromate Non-Phosphate Organic Cooling Water Treatments," *Materials Protection*, 5, No. 2, 15 (1966).

Farnsworth concludes that the organic inhibitors offer the following advantages: good corrosion and fouling protection, no waste disposal problems, acid requirement reduction, economy, and higher concentration allowances which is desirable from a cost standpoint.²²

The corrosion inhibition of copper by the use of 2-benzothiazolethiol and 2-mercaptobenzothiazole have been suggested by several authors.^{18,23} Oil-soluble sulfonates, amides, and tannin derivatives have been suggested as effective inhibitors in aluminum cooling towers. Other organic inhibitors (not specifically endorsed for cooling water inhibition) which have been described for aqueous systems are benzoate, cinnamate, salicylate, phthalate, tartrate, and ethanolamine phosphate.¹⁸

Electrochemical polarization techniques were employed by Weisstuch et al.,¹⁷ to investigate the suitability of chelating agents for cooling water inhibition. Very few chelants were satisfactory and many of them accelerated corrosion by solubilizing surface metal ions.

Chelants such as 9,10-phenanthroline and 8-hydroxyquinoline and surfactants such as lauroyl sarcosine produced measurable inhibition. It was concluded that a chelant should possess a large hydrophobic group making its surface active and the chelant should be fairly insoluble for effective inhibition.

The successful use of phosphonates to replace molecularly dehydrated phosphates for water treatment has been described by Hwa.²⁴ The widespread combined use of chromates plus polyphosphates for water treatment allows suitable inhibition at lower concentrations of chromates. The instability of polyphosphates (hydrolytic decomposition) to form metal phosphate precipitates, sludge, scale, etc., has been an undesirable characteristic of that otherwise effective treatment. Laboratory and field tests have shown that phosphonates may be substituted for polyphosphates eliminating the problems described above and with suitable inhibition results. The results of the laboratory tests are shown in Table 5.

Table 5. Comparative Corrosion Inhibition Tests in Cooling Water.*

Alloy	Corrosion Rate, mpy			
	No Inhibitor	4 ppm Na ₂ CrO ₄	8 ppm HEDDA**	Na ₂ CrO ₄ 8 ppm
Steel	15.0	11.9	14.9	2.5
Brass	3.0	2.7	2.5	1.0
Copper	2.0	2.0	1.7	0.6
Aluminum	11.0	3.4	14.0	1.8

*C. M. Hwa, "Use of Phosphates for Treating Cooling Water Systems," *Materials Protection and Performance*, 10, 12 (1971).

**Hydroxy ethylidene diphosphonic acid.

Inorganic anodic inhibitors are more widely used than organic inhibitors and will continue to be used because of their excellent inhibitive performance.²² Organic inhibitors have not been adopted extensively owing to a lack of knowledge concerning the use and mechanism of inhibition.¹⁶

PROTECTIVE FILM THEORY

Several researchers have indicated that anodic inhibition is achieved by the formation of protective insoluble films consisting largely of oxides (e.g., Fe_2O_3) on the metal surfaces.^{9,21,25} According to Pryor and Owen, the formation of a thin protective film of Fe_2O_3 approximately 200Å thick is due mainly to oxygen dissolved in the solution.²⁶ Their studies showed that powerful oxidizing inhibitors (i.e., decinormal solutions of sodium chromate and nitrite) can inhibit iron corrosion in deaerated aqueous solutions; whereas, inhibitors not containing oxidizing anions (sodium silicate, benzoate, carbonate, etc.) can inhibit iron corrosion only in aqueous solutions containing dissolved air.²⁶

ADSORPTION THEORY

The other major view of the inorganic anodic inhibitor mechanisms states that formation of an oxide film is not necessary for inhibition. According to Uhlig,⁹ inhibition by oxidizing inhibitors is primarily due to physical and activated adsorption (chemisorption) without forming definite compounds. This view has also been confirmed experimentally by other researchers.²⁵ Another theory is that inorganic inhibitors work by anodically polarizing a material.²⁵ Cartledge²⁵ states that no one mechanism can describe the inhibition action because of the many factors which influence the behavior of inorganic inhibitors.

Gatos⁹ explains the controversy concerning the anodic inhibitor mechanism as possibly caused by (1) the complexity of metallic corrosion and corrosion inhibition, (2) the variation in inhibition processes from one system to another preventing generalized studies, and (3) either or both mechanisms could be operating depending on the corrosion system of the experimental conditions.

Although a wide variety of anodic inhibitors is available, the most commonly used for cooling water treatment are the chromates, polyphosphates, nitrites, and silicates.

Although a wide variety of anodic inhibitors is available, the most commonly used for cooling water treatment are the chromates, polyphosphates, nitrites, and silicates.^{1,22,23,27,28} The inhibition characteristics of these

four anodic inhibitors are described in the following sections. Various corrosion test results are included in the data collected on these anodic inhibitors and are included for comparative purposes only. For the sake of brevity, various essential data concerning the corrosion tests (e.g., water analysis, velocity, etc.) have not been included in this report, but the reader may consult the references for the complete test conditions. Since steel is the primary metal of concern in most cooling water systems, the corrosion rates presented in the tests refer to steel unless otherwise specified.

Chromates

Chromate inhibitors are now used at Rocky Flats for corrosion control in the closed recirculating cooling water systems. The superior performance of sodium dichromate for inhibiting closed recirculating systems has been widely reported throughout industry^{21,27,30-32} and it has been equally effective at Rocky Flats. The toxicity of chromates¹ has restricted their use in the open cooling water systems at this plant because a contaminant level of 0.05 ppm hexavalent chromium cannot be exceeded in our discharge water. Contamination of surface water supplies would occur with the open systems at Rocky Flats as the result of normal "bleed off."

Chromates are used effectively in open recirculating cooling systems where local laws permit their use.^{27,30}

A solution to the problem of chromate discharge during bleed off has been presented by Kelly³³ who described two means of eliminating chromates:

1. Removal of dichromate ions from the bleed off stream with an anion exchange system.
2. Reduction of hexavalent chromium to form trivalent chromium which precipitates as chromic hydroxide. The precipitated sludge is not recoverable for inhibition reuse.

Sodium chromate, having a strong oxidizing anion, will inhibit iron corrosion in either aerated or deaerated water; whereas, inhibitors with nonoxidizing anions (e.g., silicates, orthophosphates) are only effective in aerated water.²⁶ Open recirculating cooling water systems are aerated.

Darrin's studies showed that an optimum cooling water pH range of from 7.5 to 8.5 for the use of chromate inhibitors in bimetallic systems and that sodium chromate at 500 ppm (pH 8.0) is somewhat more effective than sodium dichromate at 500 ppm (pH 5.5). Generally,

500 ppm is an acceptable level for sodium chromate treatment.³⁰ Large volume users of cooling water are using sodium dichromate plus caustic soda which is nearly as effective as chromate treatment and costs less. Comparative tests of chromate and dichromates are shown in Table 6.³⁰

Table 6. Corrosion Tests of Bimetallic Systems in Tap Water at 70°F.*

(Concentration of inhibitor equivalent to 1000 ppm of Na ₂ CrO ₄)				
Type of Panel	6 Months	18 Months	3 Years	5 Years
Iron, in contact with Brass				
In tap water	Bad	Bad	Bad	Bad
Plus bichromate	Good	Good	Excellent	Good
Plus chromate	Excellent	Excellent	Excellent	Good
Iron, contact Copper				
In tap water	Bad	Bad	Bad	Bad
Plus bichromate	Good	Good	Excellent	Excellent
Plus chromate	Excellent	Excellent	Excellent	Excellent
Iron, contact Tin				
In tap	Bad	Bad	Bad	Bad
Plus bichromate	Good	Excellent	Excellent	Good
Plus chromate	Good	Good	Good	Good
Galvanized, contact Bare Iron				
In tap water	Bad	Bad	Bad	Bad
Plus bichromate	Good	Good	Excellent	Excellent
Plus chromate	Good	Excellent	Excellent	Excellent
Galvanized, contact Brass				
In tap water	Poor	Bad	Bad	Bad
Plus bichromate	Poor	Fair	Fair	Fair
Plus chromate	Excellent	Excellent	Good	Excellent
Galvanized, contact Copper				
In tap water	Bad	Bad	Bad	Bad
Plus bichromate	Bad	Fair	Fair	Fair
Plus chromate	Good	Excellent	Good	Good
Galvanized, contact Tin				
In tap water	Bad	Bad	Bad	Bad
Plus bichromate	Excellent	Excellent	Excellent	Excellent
Plus chromate	Excellent	Excellent	Excellent	Excellent
Aluminum, contact Iron				
In tap water	Bad	Bad	Bad	Bad
Plus bichromate	Fair	Fair	Good	Good
Plus chromate	Excellent	Excellent	Good	Good

*M. Darrin, "Chromate Corrosion Inhibitors in Bimetallic Systems," *Industrial and Engineering Chemistry*, 37, 741-749 (1945).

Darrin's studies over a period of five years also examined the effect of chromate concentration as shown in Table 7.³⁰ His method of rating an inhibitor (bad, good, etc.) includes pitting data (depth, character, number) as well as weight loss measurement and Darrin considers this method as very reliable for comparing corrosion rates.

Table 7. Effect of Chromate Concentration on Corrosion.

	Chromate Concentration, ppm					
	None	62.5	125	250	500	1000
Iron Panels						
1 yr aerated	Bad	Bad	Good	Exc	Exc	Exc
2 yr nonaerated	Bad	Bad	Good	Exc	Exc	Exc
3 yr nonaerated	Bad	Bad	Good	Exc	Exc	Exc
Iron Panels, contact Brass						
1 yr aerated	Bad	Bad	Bad	Good	Exc	Exc
1 yr nonaerated	Bad	Bad	Fair	Good	Exc	Exc
3 yr aerated	Bad	Bad	Bad	Bad	Exc	Exc
Iron Panels, contact Zinc						
2 yr nonaerated	Fair	Good	Exc	Exc	Exc	Exc
3 yr nonaerated	Fair	Good	Exc	Exc	Exc	Exc
Galvanized Panels						
1 yr aerated	Bad	Good	Exc	Exc	Exc	Exc
2 yr nonaerated	Bad	Good	Exc	Exc	Exc	Exc
3 yr nonaerated	Bad	Good	Exc	Exc	Exc	Exc

Many researchers have reported deep pitting resulting from low inhibitor concentrations;^{1,14,28,32,34} however, deep pitting due to insufficient chromate inhibition did not occur in tests conducted by Sussman.³¹ He observed pits but they were broad and shallow pits. The results of his corrosion tests with chromate treated cooling tower water in the New York City area are shown in Table 8.³¹

Table 8. Corrosion Tests of Chromate-Treated Recirculating Waters.*

Equipment	Na ₂ CrO ₄ (ppm)	Exposure (days)	Corrosion Rate (mpy)
Air Washer	300	293	0.2
Indoor Cooling Tower	500	15	2.8
		23	0.6
		29	0.3
Outdoor Cooling Tower	370	26	0.7
		22	0.8
		50	0.5
Outdoor Cooling Tower	350	17	1.7
		66	0.5
Outdoor Cooling Tower	200	98	0.9
Outdoor Cooling Tower	310	26	1.0
		74	0.5

*S. Sussman, "Cooling Water Problems in the New York City Metropolitan Area," *Industrial and Engineering Chemistry*, 44, 1740-1744, August (1952).

Hess³⁵ described the severe corrosion which occurred in an open recirculating cooling water system under a phosphate treatment program. Corrosion rates were reduced to less than 5 mpy when chromate inhibitors replaced the phosphate inhibitors.

Puckorius and Ryzner obtained good correlation between corrosion rates determined with coupons and corrosion

rates measured with electrical conductivity probes in their study of chromate and polyphosphate inhibitors. Their tests showed the advantages of treated cooling water with an initial high level concentration followed by lower level maintenance treatment. Laboratory corrosion rate tests by the same researchers with various concentrations of chromate treatment are shown in Table 9.²⁸

Table 9. Corrosion Tests with Chromate-Based Inhibitors.

CrO ₄ (ppm)	Corrosion Rate (mpy)
Blank	70
100	2.0
60	2.6
30	2.8
15	4.5
7.5	10.0

At Monsanto Chemical Company, seven proprietary cooling water inhibitors were selected from a group of 28 based on laboratory test screening methods.⁸ Nitrite type and organic type inhibitors were not suitable due to high corrosion rates. The generic identification of the preferred seven inhibitors is shown in Table 10.

Table 10. Generic Identification of Selected Inhibitors.

Inhibitor	Generic Identification
1	Organo-activated chrome-polyphosphate
2	Cathodic, modified zinc dichromate (no phosphate)
3	Zinc chromate, organic (no phosphate)
4	Organo-activated zinc chromate (no phosphate)
5	Blend of inorganic materials including chromate (no phosphate)
6	Synergized blend of inhibitors predominately chromate salts
7	Chromate-polyphosphate, containing zinc

Further tests showed that although not all the straight chromate type inhibitors tested were suitable, the chromate inhibitors with added synergizers provided the best corrosion inhibition. It was observed that a low hardness, low solids type cooling water (such as we have at Rocky Flats) is the most corrosive water to steel and is the most difficult to inhibit.

Uhlig summarized the limitations of chromate treatments as follows:¹

1. Severe pitting results from insufficient inhibitor concentrations.
2. If organic reducing matter is present in the cooling water, chromates may be reduced to chromic salts which do not inhibit corrosion.

3. The toxicity of chromates may restrict their use.

The inhibition of cooling water through the use of less toxic organic chromates has been studied by several investigators.^{20,24} Shields, et al.,²⁹ described screening tests of 50 different inhibitors which resulted in the selection of organic chromates as the optimum cooling water inhibitor. Inorganic chromates provided suitable protection; but, due to handling hazards and disposal problems, the less toxic organic chromates were selected. Other inhibitors screen tested included simple phosphates, polyphosphates, polyphosphates plus chromates, inorganic and organic chromates, ethylene diamine tetraacetic acid salts, borates and borate mixtures, zinc promoted mixtures, and oils. During two years in operation on a plant scale, the effectiveness of organic chromates complemented with 2 ppm hexametaphosphate resulted in corrosion rates averaging 1 mpy.²⁹

Shields summarized other advantages, besides being less toxic, of organic chromates compared to inorganic chromates:

1. Organic chromates possess lower chromium contents and more favorable molecular structure.
2. Lower concentrations of organics provide protection equivalent to the inorganic chromates.
3. Less pitting is produced by organic chromates.

Whitney³⁶ reported excellent results with organic chromates using 13 ppm residual chromate inhibitors. The results of his comparative cooling tower tests are shown in Table 11.

Table 11. Comparative Corrosion Test Results.*

Inhibitor	Test Number	Corrosion Rate (mpy)	Remarks
Organic Chromate	1	<1	No visible attack.
Organic Chromate	2	<1	One anodic area, remainder free from attack.
Organic Chromate	3	<1	No visible attack.
Phosphate Treatment 15 ppm	4	10	Severe non-uniform attack, bulky coating.

*F. L. Whitney, Jr., "Inhibiting a Cooling Water Tower System," *Corrosion*, 13, 711t (1957).

Whitney described the adverse effects of inadequate controls and, although excellent results were obtained with organic chromates, further efforts were being made to select a more economical treatment.

Phosphates

Polyphosphates (sodium phosphate glasses) are commonly used for corrosion control in recirculating cooling water systems.^{22,23,28,32,37} Although phosphates are anodic inhibitors, several researchers have observed that localized corrosion (pitting) does not occur at low concentrations, in contrast to the behavior of the chromates.^{32,38} Kahler's tests, however, showed severe pitting tendencies for mild steel in phosphate-treated water with low concentrations (0 to 10 ppm) at pH 7 to 9 and at high concentrations (10-100 ppm) at pH 5.5 to 7.³⁴ Hatch described the increased corrosion of steel exposed to highly concentrated solutions of sodium phosphate glasses.⁴ Ryzner indicates that pitting due to low concentrations of inhibitors is more severe with chromates than with phosphates.²⁸ Pryor and Cohen showed the effect of an inhibitor concentration on the corrosion rate of steel.²⁶ It is seen in Figure 1 that insufficient quantity of inhibitor does accelerate corrosion attack.

Figure 1. Accelerated Corrosion Caused by Insufficient Inhibitor Concentration. (M. J. Pryor and M. Cohen, "The Inhibition of the Corrosion of Iron by Some Anodic Inhibitors," *Journal of the Electrochemical Society*, 100, 5 [1953]).

Polyphosphate concentrations of 25 to 50 ppm are generally used for corrosion prevention. They are most effective when the water pH is between 5 and 7. When the pH is greater than 7, the polyphosphates provide less effective inhibition and tuberculation may occur.^{32,39} Several authors emphasized that, to maintain inhibition, the ratio of polyphosphates to calcium hardness expressed as CaCO_3 must be less than two.^{4,23}

Farnsworth indicated the limitations of polyphosphate treatments as:²²

1. Phosphates are not recommended in systems with high calcium content because of calcium phosphate precipitation.
2. High system temperatures or long holding times can cause reversion of polyphosphate to orthophosphates resulting in loss of inhibition and phosphate deposition.

Brandel also described the detrimental deposition of phosphate scale at high inhibitor concentrations.³²

Puckorius' corrosion tests with polyphosphate-based inhibitors showed the effect of inhibitor concentration on the corrosion rate and the advantages of high level start up treatment followed by low level maintenance. The results of these tests are shown in Table 12.²³

Table 12. Corrosion Rate Test Results (14 day tests).

PO_4 Concentration (ppm)	Corrosion Rate (mpy)	Total Deposition (mg/cm^2)
60 ppm - 4 days	0.6	2.0
20 ppm - 10 days	0.6	2.0
60 ppm - continuously	1.0	1.4
20 ppm - continuously	49.0	33.7

Cooling tower tests performed at Monsanto Chemical Company showed the inhibition provided by the metallic phosphates was equivalent to the effectiveness of the chromate treatment. The test results are summarized in Table 13.

Table 13. Comparative Cooling Tower Test Results.

Treatment	Exposure Period (days)	Corrosion Rate (mpy)	Remarks
City water only	28	7	Rust film on 30-40% of sample. Anodic attack, depth 1 mil.
Plant recirculated water, phosphate 24 ppm	28	6	40% rusted, hard scale. Severe anodic attack, depth 8 mils.
Plant recirculated water, Inhibitor A, chromate, 24 ppm	28	<1	Slimy film easily washed off. No difference in appearance from first week.
Plant recirculated water, metallic phosphate 56-46 ppm	7	1	Slimy film, one pit in stencil mark.
	14	<1	
Plant recirculated water, metallic phosphate 24-34 ppm	12	<1	Slimy film easily removed. Appreciable anodic attack, depth 1½ mils, pitting 1 mil.

The beneficial effect of the addition of zinc salts to polyphosphates has been thoroughly discussed by several researchers.^{15,37,40} Hatch has stated that the inclusion of zinc in a polyphosphate treatment accelerates a protective film formation, lowers the total level of inhibition concentration, and improves film repair. The polyphosphate inhibitive process is not affected by zinc which provides rapid protection until the slower acting polyphosphates can form a protective film.³⁹

Bregman observed that the addition of cobalt, cerium, chromium, manganese, cadmium, lead, tin, and nickel cations also improves polyphosphate inhibition; whereas, uranium, beryllium, iron, strontium, thallium, copper, aluminum, antimony, and zirconium cations accelerate corrosion.³⁷ Bregman's results showing the beneficial effect of the addition of ferrocyanide to polyphosphates are depicted in Figure 2.³⁷

*J. I. Bregman and T. R. Newman, "Developments in Cooling Tower System Treatments," *Corrosion*, 15, 97t (1959).

Figure 2. Synergizing Effect of Ferrocyanide on Polyphosphate Treatment.*

Hatch and Rice, using agitated batch tests,⁴¹ showed how the corrosion of steel in tap water is affected by the concentration of sodium phosphate glasses (sodium hexameta-phosphate). As the inhibitor concentration approached 100 ppm, the inhibitors became more effective. Weight losses rapidly increased above 100 ppm until the corrosion rate exceeded that of untreated tap water showing that high concentrations of glasses are definitely corrosive to steel. The inhibitive effect of Calgon on dissimilar coupled metals was shown in further tests by Hatch.⁴² The effects of temperature, pH, velocity, and volumetric rate of flow as factors in protective film development were also covered in this study. Threshold treatment with the glassy phosphates

also is effective in controlling corrosion of zinc, copper, brass, and aluminum as well as steel. In further dissimilar metal studies (copper-steel), Hatch described the inhibitive properties of 2-benzothiazole plus a zinc bearing phosphate glass (Calgon T) inhibitor. This combination of inhibitors effectively prevents copper pickup (a common problem in copper-steel recirculating systems where dissolved copper plates out on steel setting up a galvanic cell) and effectively protects the steel in the water system.⁴⁰

Several authors indicated that polyphosphates are superior to orthophosphates for corrosion inhibitors in cooling water systems.^{34,37,43} Bregman states that the superior corrosion inhibition of the polyphosphate is due to greater tendency to minimize scaling, and lesser tendency to form calcium phosphate sludge. Reversion of the polyphosphates to orthophosphates does occur with time, and analysis of cooling tower water will show reversion of 50 to 75% of the polyphosphates to orthophosphates.²³ Another problem in the reversion to the ortho form is the resulting production of insoluble iron phosphates. Hatch states, however, that the presence of moderate amounts (up to 50%) of ortho-phosphates with polyphosphates enhances common inhibitors and aids in protective film formation.³⁹ Other researchers have stated that the reversion of the polyphosphate to orthophosphate is reduced at lower temperatures.⁴³

The effectiveness of a combination of chromates and phosphates (dianodic treatment), which provides better inhibition than either inhibitor used separately, has been described by several authors.^{31,33} The results of tests conducted by Kahler showing pitting reduction by dianodic treatment are shown in Figure 3.³⁴

Reduced weight loss was also observed for the dianodic treatment but reduced pitting was the major improvement.

Polyphosphate inhibitors are widely used in most open recirculating cooling water systems to control scale deposition with low inhibitor concentrations of 1-5 ppm (called threshold treatment).

Nitrites

Uhlig states that chromates and nitrites are the most efficient inhibitors for controlling iron and steel corrosion although toxicity has restricted their use.²⁷ Hoar has listed some advantages and disadvantages of nitrite inhibitors as:⁴⁴

1. Nitrites are less active with organic materials than chromates.
2. Nitrites are much less toxic than chromates.

Figure 3. Reduction of Pitting by Dianodic Treatment.

3. Nitrites generally cost less than chromates.
4. Nitrites are colorless.
5. Nitrites cannot be used where the water system pH is below 6.5.
6. Nitrites may be destroyed by micro-organisms; chromates tend to destroy micro-organisms.

Toar noted that the mechanism of nitrite inhibition is similar to chromate inhibition but not as fully understood.

The results of laboratory tests by Sussman showed that the presence of high sulfate and chloride concentrations adversely affected the inhibitive properties of sodium nitrite.⁴⁵

The results of field tests employing sodium nitrite inhibitors are shown in Table 14.

The variable corrosion rates indicate that further study of nitrites is necessary to make the nitrites a useful inhibitor. Sussman describes ineffective nitrite inhibition of non-ferrous metals under conditions which protect steel. The necessary addition of auxiliary inhibitors which improve nitrite inhibition for cooling waters could result in prohibitive costs.⁴⁵

Table 14. Corrosion Tests Showing Variations in Corrosion Rates.

Unit*	Average Circulating Water Analyses			Exposure (days)	Corrosion Rate (mdd)
	NaNO ₂ (ppm)	Cl (ppm)	SO ₄ (ppm)		
<u>Steel</u>					
AW	1231	6	33	56	43.0
	480	21	85	42	12.2
	1077	4	21	29	0.0
	1620	5	23	74	0.0
<u>Steel</u>					
AW	850	21	128	70	30.0
	586	44	220	30	26.1
	2312	113	341	57	32.6
CT	4951	114	319	86	7.7
AW	1130	32	173	58	4.0
	3985	73	385	30	0.0
<u>Aluminum</u>					
AW	2320	163	675	57	31.7
	700	22	67	13	4.7
	268	7	28	13	0.0

*AW = air washer
CT = cooling tower

Silicates

Various forms of sodium silicates have been employed to prevent water corrosion of steel since the early 1920's. The addition of low levels of non-toxic sodium silicate has been effectively used to control corrosion in potable water pipes.^{46,47} The silicates have not been used as extensively as chromates and phosphates for inhibiting cooling water systems.⁴⁸ Sodium silicate has been recommended by the American Society of Refrigeration Engineers for inhibiting recirculating water.¹ The results of laboratory tests with recirculating water exposed to air showed the following inhibitors listed in descending order of effectiveness: sodium chromate (or dianodic), sodium silicate, sodium phosphate.¹

Various views have been expressed concerning the mechanism of silicate inhibition; however, studies by Lehrman and Shuldener have confirmed that silica does form absorption compound with existing corrosion products in the water system (no protective film will form until some corrosion products are present) which also prevents excessive film deposit.⁴⁷

The film formed is described as a two layer deposit with the lower layer composed of corrosion products. The upper layer is a conglomerate adsorption compound of silica-metal hydroxide and silica gel.⁴⁸ The inhibition effectiveness of water soluble silica has been classified by Stericker as follows:

1. Crystalloid silica — good corrosion inhibitive properties.
2. Stable hydrated colloidal silica — better inhibitive properties than crystalloid silica.
3. Unstable hydrated colloidal silica — poor.

Wood et al.⁴⁶ described the effective inhibition of a wide variety of cooling waters with a treatment of 30 to 40 ppm crystalloid silica. Wood stated that water with a high pH (8.6) should be adjusted with mineral acid before being treated with silicate inhibitors. Sussman, however, obtained excellent inhibition using silicates in recirculating water systems with high pH.³¹

Several authors have stated that silicate inhibitors will provide corrosion inhibition for lead, brass, copper, zinc, and aluminum, as well as iron and steel.^{1,48,49}

Wood indicates that high level treatment (70 ppm) is necessary at the inception of treatment for several weeks to accelerate initial formation of protective films with subsequent maintenance levels held at 35 ppm.

Comparative cooling water tests were conducted by Monsanto Chemical Company for selection of a suitable water treatment program.³⁶ Following a literature survey, laboratory tests were conducted on three types inhibitors: sodium silicate, chromates, and phosphates. Following the laboratory tests, cooling towers were treated with the three inhibitors with the results shown in Table 15.

Table 15. Cooling Tower Corrosion Test Results.*

Inhibitor	Corrosion Rate (mpy)	Appearance of Surface
Phosphate (10-15 ppm metaphosphate residual)	15	Covered with soft, bulky coating. Cleaned sample shows severe cratering, anodic, and pitting at attack.
Sodium Silicate (100-150 ppm silicate residual)	12	Covered with very hard, fairly dense coating.
Sodium Dichromate (150-200 ppm chromate residual)	2	Very clean surface and thin film covering.

*F. L. Whitney, Jr., "Inhibiting a Cooling Water Tower System," *Corrosion*, 13, 711t (1957).

Improved inhibition was obtained by increasing the silicate concentration from 8-10 ppm used in the laboratory tests up to 100-150 ppm for the cooling tower tests; however, excessive pitting occurred in the tower tests. The author

concluded that optimum inhibition was obtained using organic chromates or metallic phosphates.

Sussman states that the problem of silicate scale formation may be eliminated by close controls and his results of cooling tower tests showed that silicates were nearly as effective as chromates. Typical silicate treated cooling tower tests results are shown in Table 16.

Table 16. Cooling Tower Corrosion Test Results.

Equipment	SiO ₂ (ppm)	Exposure (days)	Corrosion Rate (mpy)
Air Washer	80	252	1.9
Indoor Cooling Tower	184	15	2.8
		22	1.3
		36	0.6
Outdoor Cooling Tower	51	8	2.5
		34	1.0
		50	0.7

Some of the factors governing the use of silicates for inhibition have been summarized by Stericker:⁵⁰

1. The minimum sodium silicate concentration level necessary for inhibition is 8 ppm.
2. Higher concentrations of silicates are needed during initial treatment for protective film formation.
3. After a protective film has formed, a minimum silicate concentration level of 4 ppm is suitable.
4. Silicates with the formula Na₂O:3.3 SiO₂ are best suited for waters with a pH over 6.0.
5. Higher silicate concentrations are necessary for high chloride content waters.
6. Stagnant areas of water are rapidly depleted of silica which allows for more rapid corrosion in the unprotected areas. Sufficient inhibitor concentration is necessary.
7. Bimetallic systems have been protected with silicates.

A NACE publication states that close control of pH is necessary for silicate inhibition because inhibition efficiency is decreased above 7.5 and below 6.5 pH. A concentration level of 20 to 40 ppm was recommended for corrosion control. Higher concentrations are not recommended due to possible build up of calcium silicates on heat transfer surfaces.⁵¹

Sodium silicate has provided excellent corrosion inhibition for mild steel in preliminary open cooling water tests conducted at Rocky Flats as shown in Table 17.⁵²

Table 17. Cooling Tower Corrosion Tests.

Tower	Corrosion Inhibitor Type	Corrosion Rates, 30 days (mpy)	Appearance of Sample Surface
A	Untreated	7.4 7.6	Heavy rust, pitting
B	Polyphosphate	0.3 0.4	Clean surface, no pits
C	Polyphosphate	2.6 2.8	Slimy film, pitting, Tubercules
D1	Polyphosphate plus sulfamic acid pH control	3.4 3.4	Tubercules, severe pitting
D2	Sodium Silicate (water glass-41° Be'), 70 ppm SiO ₂	0.3 0.4	Slight film, no pitting

When sodium silicate (water glass- $\text{Na}_2\text{O} \cdot 3.3 \text{SiO}_2$) was substituted for a polyphosphate treatment in Tower D, the corrosion rate was reduced from 3.4 mpy to <1 mpy and the tuberculation and pitting (which was observed for the polyphosphate treatment) was eliminated. Further cooling tower tests will be conducted to determine the effectiveness of silicate inhibition in other open cooling water systems where improved inhibition is necessary.

Bischof and Goldstein have compiled a list of corrosion inhibitors describing the possible restriction of their use by pollution control standards. Of the commonly used inhibitors, only silicates were listed as being unaffected by present or future pollution laws as shown in Table 18.⁵³

CONCLUSIONS

This survey of the literature has drawn upon a broad background of industrial experience in the use of metallic

corrosion inhibitors for recirculating cooling water systems. The data presented by previous investigators should be helpful in the selection of inhibitors for effective water treatment.

It is evident from the literature and from the effective performance of chromates at Rocky Flats that the use of chromates for treating the closed recirculating cooling water systems should be continued at this plant. The toxicity of chromates which restricts their use in open water systems is not a factor in the closed recirculating water systems where bleed off or discharge to surface waters does not occur.

Preliminary tests of the open recirculating water systems at Rocky Flats indicate that some of the open cooling water systems are being effectively inhibited against metallic corrosion; but, metallic corrosion is still a problem at several other areas. The use of sodium silicates inhibition has provided improved corrosion control in one open recirculating system. Further laboratory tests and cooling tower site tests are now being conducted to select other inhibitors which may provide improved water treatment where needed.

REFERENCES

1. H. H. Uhlig, "The Corrosion Handbook," John Wiley & Sons, Inc., New York (1948).
2. J. N. Breton, "Corrosion Control with Organic Inhibitors," *Industrial and Engineering Chemistry*, 44, 1755-1761 (1952).
3. C. E. Knapp, "Cooling Towers Boost Water Reuse," *Environmental Science and Technology*, 5, 204 (1971).
4. G. B. Hatch and O. Rice, "Threshold Treatment of Water Systems," *Industrial and Engineering Chemistry*, 37, 710-715 (1945).

Table 18. Effect of Pollution Controls on the Use of Inhibitors.

Inhibitors Presently Affected	Inhibitors Probably to be Affected	Inhibitors Not Affected
Chromates	Polyphosphate	Silicates
Chromate-Zinc	Polyphosphate-Zinc	Acid-alkali addition for Langelier or Ryzner Index Control
Polyphosphate-Chromate	Organo-Phosphonate-Zinc	
Polyphosphate-Chromate-Zinc	Lignosulfonate-Zinc	
Organo-Phosphonate-Chromate-Zinc	Bioflavonoid-Zinc	
	Polyphosphates-Silicate	
Polyphosphate-Ferrocyanide	Silicate-Nitrites (Nitrates)	
Polyphosphate-Ferrocyanide-Zinc	Molybdate-Polyphosphate-Zinc	
Molybdate-Chromate-Zinc		
Molybdate-Polyphosphate-Chromate	Mercaptobenzoithiozole	
	Phosphate Ester-Zinc	
Bioflavonoid-Chromate-Zinc	Silicate-Phosphate Ester	
	Silicate-Organo-Phosphonate	
Lignosulfonate-Chromate-Zinc		
Phosphate Ester-Chromate-Zinc		
Organic Chromate-Polyphosphate		

5. G. Rey, W. J. Lacy, and A. Cywin, "Industrial Water Resue: Future Pollution Solution," *Environmental Science and Technology*, T60 (1971).
6. R. J. Malley and K. E. Gaspar, "Bleed-Off is Essential in Preventing Corrosion and Scale in Recirculating Water Systems," *Materials Protection*, 3, 10 (1964).
7. Analytical Laboratory Water Analysis Reports, April 5, 1971, and October 25, 1971, Rocky Flats Division, Dow Chemical U.S.A.
8. A. O. Fisher, "Laboratory Evaluation of Fresh Cooling Water Inhibitors for Open Recirculating Systems," *Materials Protection*, 1, 10 (1962).
9. H. C. Gatos, "Inhibition of Metallic Corrosion in Aqueous Media," *Corrosion*, 12, No. 1, 39 (1956).
10. NACE Technical Committee Reports, "Some Corrosion Inhibitors - A Reference List," Publication 55-3, *Corrosion*, 11, 4, 65 (1955).
11. E. L. Miller, "How to Conduct an In-Plant Water Treatment Training Program," *Maintenance Engineering*, 21, No. 2, February 1971.
12. M. G. Fontana and N. D. Greene, "Corrosion Engineering," McGraw-Hill Book Company (1967).
13. R. V. Jelinck, "How Environment Directs Corrosion Control," *Chemical Engineering*, 65, No. 19, 163 (1958).
14. U. R. Evans, "Use of Soluble Inhibitors," *Industrial and Engineering Chemistry*, 37, 703-706 (1945).
15. R. S. Thornhill, "Zinc, Manganese, and Chromic Salts as Corrosion Inhibitors," *Industrial and Engineering Chemistry*, 37, 706-709 (1945).
16. J. N. Breton, "Corrosion Control with Organic Inhibitors," *Industrial and Engineering Chemistry*, 44, 1755-1761 (1952).
17. A. Weissstuch, D. A. Carter, and C. C. Nathan, "Chelation Compounds as Cooling Water Corrosion Inhibitors," *Material Protection and Performance*, 10, No. 4, 11 (1971).
18. M. G. Fontana and R. W. Staehle, "Advances in Corrosion Science and Technology," Plenum Press, New York (1970).
19. L. C. Rowe, "An Evaluation of Inhibitors for Corrosion Prevention in an Engine Cooling System," *Corrosion*, 13, 750t (1957).
20. J. I. Bregman and D. B. Boies, "Laboratory Testing of Railroad Diesel Cooling System Inhibitors," *Corrosion*, 14, 275t (1958).
21. U. R. Evans, "The Corrosion and Oxidation of Metals," Edward Arnold Publications, London (1960).
22. N. B. Farnsworth and R. S. Robertson, "Non-Chromate Non-Phosphate Organic Cooling Water Treatments," *Materials Protection*, 5, No. 2, 15 (1966).
23. A. J. Haygood and J. D. Minford, "Aluminum Cooling Towers and Their Treatment," *Corrosion*, 15, 20t (1959).
24. C. M. Hwa, "Use of Phosphates for Treating Cooling Water Systems," *Materials Protection and Performance*, 10, 12 (1971).
25. G. H. Cartledge, "Recent Studies of the Action of Inorganic Inhibitors," *Corrosion*, 18, 316t (1962).
26. M. J. Pryor and M. Cohen, "The Inhibition of the Corrosion of Iron by Some Anodic Inhibitors," *Journal of the Electrochemical Society*, 100, 5 (1953).
27. H. H. Uhlig, "Corrosion Control in Water Systems," *Industrial and Engineering Chemistry*, 44, 1736-1740 (1952).
28. P. R. Puckorius and W. J. Ryzner, "Cooling Water Inhibition Performance," *Corrosion*, 16, 473t (1960).
29. H. Shields, L. V. Sorg, and R. L. Stutz, "Selecting Corrosion and Scale Inhibitors for Cooling Water," *Corrosion*, 15, 233t (1959).
30. M. Darrin, "Chromate Corrosion Inhibitors in Bimetallic Systems," *Industrial and Engineering Chemistry*, 37, 741-749 (1945).
31. S. Sussman, "Cooling Water Problems in the New York City Metropolitan Area," *Industrial and Engineering Chemistry*, 44, 1740-1744, August (1952).
32. A. J. Brandel, "Recirculation of Cooling Water in Petroleum Refining," *Industrial and Engineering Chemistry*, 48, 2156 (1956).
33. B. J. Kelly, "Cooling Tower Chromates-Recovery or Disposal," *Materials Protection*, 8, No. 3, 23 (1969).
34. H. L. Kahler and P. J. Gaughan, "Protection of Metals Against Pitting, Tuberculation, and General Corrosion," *Industrial and Engineering Chemistry*, 44, 1770-1774 (1952).
35. W. A. Hess, "Refining Corrosion Rates Below 5 mpy Achieved by Chromate Water Treatment," *Corrosion*, 16, (1960).
36. F. L. Whitney, Jr., "Inhibiting a Cooling Water Tower System," *Corrosion*, 13, 711t (1957).
37. J. I. Bregman and T. R. Newman, "Developments in Cooling Tower System Treatments," *Corrosion*, 15, 97t (1959).
38. G. B. Hatch, "Protective Film Formation with Phosphate Glasses," *Industrial and Engineering Chemistry*, 44, 1780-1786 (1952).
39. G. B. Hatch, "Polyphosphate Inhibitors in Potable Water," *Materials Protection*, 8, No. 11, 31 (1969).
40. G. B. Hatch, "Control of Couples Developed in Water Systems," *Corrosion*, 11, 461t (1955).
41. G. B. Hatch and O. Rice, "Corrosion Control with Threshold Systems," *Industrial and Engineering Chemistry*, 37, 710-715 (1945).

42. G. B. Hatch, "Inhibition of Galvanic Attack of Steel with Phosphate Glass," *Industrial and Engineering Chemistry*, 44, 1780-1786 (1952).
43. A. O. Fisher and J. R. Jeter, "Correlation of Lab and Field Data on Five Corrosion Inhibitors for Recirculating Water Systems," *Materials Protection*, 3, No. 5, 10 (1964).
44. T. P. Hoar, "Nitrite Inhibition of Corrosion: Some Practical Cases," *Corrosion*, 14, 103t (1958).
45. S. Sussman, O. Nowakowski, and J. J. Constantine, "Experiences with Sodium Nitrite Unpredictable Corrosion Inhibitor," *Industrial and Engineering Chemistry*, 51, 581-584 (1959).
46. J. W. Wood, J. S. Beecher, and P. S. Laurence, "Some Experiences with Sodium Silicate as a Corrosion Inhibitor in Industrial Cooling Waters," *Corrosion*, 13, 719t (1957).
47. L. Lehrman and H. L. Shuldener, "Action of Sodium Silicate as a Corrosion Inhibitor in Water Piping," *Industrial and Engineering Chemistry*, 44, 1765-1769 (1952).
48. H. L. Shuldener and S. Sussman, "Silicate as a Corrosion Inhibitor in Water Systems," *Corrosion*, 16, 354t (1960).
49. B. A. Wilson, "Identification of Inhibition Films on Aluminum in Silicate Solutions," *Corrosion Science*, 11, (1971).
50. W. Stericker, "Protection of Small Water Systems from Corrosion," *Industrial and Engineering Chemistry*, 37, 716-721 (1945).
51. TPC Publication Number 1, "Cooling Water Treatment Manual," National Association of Corrosion Engineers, Houston (1971).
52. J. L. Briggs, Private communication (1971).
53. A. E. Bischof and P. Goldstein, "Chemical Treatment for Cooling Tower and Related Systems," *Materials Protection and Performance*, 10, 12 (1971).