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# CORROSION INHIBITORS

## Manufacture and Technology

Maurice William Ranney

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**Maurice William Ranney**

**NOYES DATA CORPORATION**

**Park Ridge, New Jersey**

**London, England**

**1976**

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## FOREWORD

The detailed, descriptive information in this book is based on U.S. patents issued since mid-1972 and relating to corrosion inhibitors. This includes four patent applications published in early 1975.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced, technically oriented review of substances that prevent or retard the deterioration of materials prone to corrosion.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas to research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring our new durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

## 15 Reasons Why the U.S. Patent Office Literature Is Important to You —

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source.
2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."
3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.
4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.
5. Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.
6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.
7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.
8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.
9. Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.
10. Obtain licenses — many U.S. chemical patents have not been developed commercially.
11. Patents provide an excellent starting point for the next investigator.
12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.
13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.
14. Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.
15. It is a creative source of ideas for those with imagination.

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## INTRODUCTION

The use of organic antidegradants is well known. Many types of organic compounds have been suggested for use in this connection. They may be ionized compounds such as carbonates, certain benzoates and the like, or nonionized compounds such as aldehydes, amines, thiols, sulfides, thioureas and the like or certain aromatic amines and certain phenols.

The term antidegradant includes within its meaning properties which inhibit corrosion as well as properties which stabilize or adjust the environment in which it has been applied. Known corrosion inhibitors frequently function primarily to form a protective barrier on the surface of a substrate by physical adsorption, chemisorption or reaction with the substrate. An antidegradant may or may not perform the same function or may mainly stabilize or alter the bulk environment. To illustrate, corrosion problems may manifest themselves in the operation of the automobile by: the degradation of lubricating oils and greases and the corrosion of metal-bearing surfaces lubricated thereby; the degradation of fuel and the corrosion of fuel-receiving combustion chamber walls; the corrosion of the walls of a combustion by-product transmitting exhaust system; the failure of a degraded hydraulic system fluid and the corrosion of surfaces in contact therewith; and the degradation of a transmission fluid and the corrosion of surfaces in contact therewith.

Working fluids, which include natural and synthetic organic oils, greases and fuels are susceptible to degradation, especially under the severity of conditions in which they are utilized. The myriad uses of these working fluids impose working conditions which cause degradation either to them or to the substrate with which they are in contact. Inasmuch as losses attributable to degradation amount to billions of dollars annually, much effort is being devoted to the preparation of more efficient additives by incorporating some or all of the above antidegradant properties in one, or a mixture of, compounds(s) which may be capable of interacting with the surface of the metal and also be capable of acting as environment stabilizers or alterers.

This book provides a review of the recent R & D effort directed toward the solution of this most persistent and relentless problem—corrosion. Over 260 processes relating to all phases of corrosion control in industrial, automotive, aircraft and other such specialized areas of concern are described in detail. While many additives and preventive techniques are fully satisfactory for a number of end uses, the arrangement here reflects the most significant and practical aspects of each process.

## COOLING WATER, BOILERS AND WATER SUPPLY PLANTS

Corrosion of metals in contact with a water system involves an electrochemical attack. For this attack to occur, a potential difference must exist between one part of the structure and another. The primary reaction in the region at the lower potential, i.e., the anode, is the dissolution of metal in the form of ions. The electrons liberated by this reaction migrate through the metal and are utilized in the reduction of either ions or oxygen. The overall effect is the passage of a current through the circuit formed by metal and solution, the current carriers being electrons in the metal and dissolved ions in the solution. Corrosion-inhibitors are useful in such systems as domestic water supply systems, circulating water systems for cooling or air conditioning, steam-generating plants, condensers, refrigerating brines, and acid pickling systems.

In preventing local attack or general corrosion, inhibitors serve a number of desirable functions. They avoid the blockage of pipes by corrosion products, keep the water clean for biological or esthetic reasons and maintain optimum conditions for heat transfer. The latter characteristic may be just as important as the reduction in corrosion products. The ability to maintain good pumping capacity in a pipe may mean an appreciable saving in cost because the design diameter can be smaller than is the case if allowance has to be made for roughness and reduction in diameter caused by build-up of corrosion products.

Effective corrosion-inhibiting treatment of such systems is made difficult by the geometry of the system, the large capacity, dissimilar metals present, and by other variable factors, such as salt and oxygen content, flow velocity, temperature and volume of make-up.

A large amount of study of corrosion over the last thirty years has produced a store of knowledge relating to corrosion-inhibition. Inorganic compositions such as chromates, dichromates, nitrites, silicates, phosphates and carbonates have been used successfully as corrosion-inhibitors. Both chromates and dichromates are widely used under service conditions and are very effective when properly applied. Owing to their toxicity however, their use is restricted to industrial waters and may have to be eliminated entirely in view of ecological considerations.

Sodium nitrite is an effective inhibitor for iron and a number of other metals in a wide variety of water ranging from fresh water up to brackish water and seawater. A high percentage of nitrite is needed as the sodium chloride content of the water to be treated increases. Also, bacteria can readily oxidize nitrite to nitrate which has no corrosion-inhibiting action. Polyphosphates and silicates behave in a similar way in the treatment of waters; they both tend to buffer on the alkaline side of neutrality, and both require the presence of oxygen.

Organic compounds such as sodium and potassium benzoate, monoethanolamine benzoates and salicylates, and alkylphosphonic acids are known to inhibit metal corrosion. Sodium mercapto-benzothiazole and benzotriazole have been known as effective corrosion-inhibitors for copper, copper alloys and other nonferrous metals and alloys. In recent years, increasing emphasis has been placed on the use of organic corrosion inhibitors.

In addition to corrosion problems, cooling water systems are subject to other difficulties, depending upon impurities present in the water. For example, if the cooling water is vaporized, scale formation may be a problem; this problem can be avoided by softening the water, e.g., by ion exchange treatment or by precipitating the scale formers, by adding a sequestering agent such as a lignosulfonate, an inorganic polyphosphate, an organophosphonate or a polysilicate of the type formed by a sodium silicate, or, as suggested in U.S. Patent 3,492,240, by adding hydrolyzed polyacrylonitrile or, as suggested by French Patent 1,550,452, by adding polymethacrylic acid or an alkali salt thereof.

It is frequently desirable to add a biocide to cooling water, e.g., to inhibit the growth of algae therein. Water from the available source may also contain silt, which can cause serious loss of heat exchange efficiency unless its deposition on heat exchanger surfaces is prevented. This can be accomplished by using certain lignosulfonate dispersants or, preferably polyelectrolytes, in particular, polyacrylics: see, for example, *General Deposit Control Mechanisms*, William H. Hales, Special Report presented at International Water Conference, 13th Annual Meeting, William Penn Hotel, Pittsburgh, Pa., October 28-30, 1969.

In addition, water from the available source may contain oil contamination, and detergents used to emulsify such contamination. Various pH control agents are often added to cooling water systems to neutralize acid or alkali substances picked up by the circulating water.

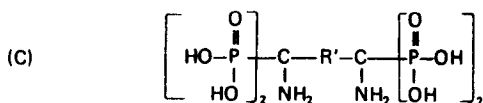
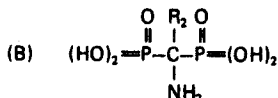
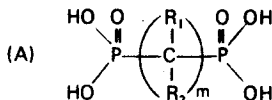
The treatment of the water in cooling water systems is a continuing problem, because chemicals added to the systems may be lost as a consequence of chemical reactions that are involved in their performance of the desired function, because the chemical composition of the cooling water is changed as a consequence of its actual use, because make-up water must be added to the system from time to time, thereby diluting the entire system, because cooling water is periodically or continually removed from the system to prevent salt build-up, or for a combination of these and other reasons.

Accordingly, it is necessary to monitor any given cooling water system periodically, and to make appropriate additions of treating chemicals. The frequency of the monitoring and addition varies drastically from system to system, and may be measured in months, weeks, days or hours: in extreme cases, continuous monitoring may be required.

## COOLING WATER

### Alkylene Polyphosphonic Acid, Azole and Zinc Salts

C.M. Hwa; U.S. Patents 3,803,047 and 3,803,048; April 9, 1974; both assigned to W.R. Grace & Company describes a corrosion-inhibiting composition which consists essentially of from 1 to 80 weight percent of an alkylene polyphosphonic acid having one of the following formulas (A), (B) or (C):



where  $m$  is an integer from 1 to 10,  $R_1$  is hydrogen, or an alkyl group having from 1 to 4 carbons and  $R_2$  is hydroxyl, hydrogen, or an alkyl group having from 1 to 4 carbons,  $R_3$  is an alkyl group having 1 to 10 carbons, benzyl or phenyl,  $R'$  is an aliphatic radical having from 1 to 10 carbons, and the water-soluble salts and esters thereof; or mixtures thereof, and from 1 to 80 weight percent of an azole compound selected from a group consisting of triazoles, pyrazoles, imidazoles, isoxazoles, oxazoles, isothiazoles, thiazoles and mixtures thereof, and/or from 1 to 95 weight percent of a water-soluble zinc salt.

The compositions are useful for treating a variety of aqueous systems, that is, any aqueous system corrosive to metal surfaces. Suitable systems which can be treated include water treatment systems, cooling towers, water circulating systems, and the like where fresh water, brines, seawater, sewage effluents, industrial wastewaters, and the like are circulated in contact with metal surfaces. These compounds are useful in acid pickling baths, radiator coolers, hydraulic liquids, antifreezes, heat transfer mediums, and petroleum well treatments. The process is suitable for reducing the corrosion of iron, copper, aluminum, zinc and alloys containing these metals such as steel and other ferrous alloys, brass, and the like which are in contact with corrosive aqueous systems.

**Example 1:** This example demonstrates the synergistic reduction in corrosion rates obtained with the compositions of this process. In this test, circulating water having the following composition was used:

Calcium sulfate dehydrate	445 ppm
Magnesium sulfate heptahydrate	519 ppm
Sodium bicarbonate	185 ppm
Calcium chloride	136 ppm

During the test, the circulating water was fed to a closed circulating test system at a rate of 5 gallons per day, the overflow from the test system being discharged to waste. In the closed circulating system, circulating water having a temperature of 130°F and pH of 6.5 to 7.0 was fed at a rate of 1 gal/min to a coupon chamber containing test coupons for the corrosion test.

Water from the coupon chamber was then passed through an arsenical admiralty brass tube surrounded by a jacket through which a heating fluid having an initial temperature of 240°F was countercurrently passed. The circulating water was then cooled to 130°F and recirculated through the system. The total circulating time for each test was 10 days.

Mild steel, brass (33 wt % zinc), copper and aluminum coupons having an average area of 26.2 cm<sup>2</sup> were used in the test chamber. The coupons were carefully cleaned and weighed before use. Following the test, each coupon was cleaned with inhibited hydrochloric acid, rinsed, dried and weighed to determine the corrosion rate in mils per year. A comparison of the corrosion rates of the individual ingredients of the composition of this process with combinations of these ingredients according to this process were found to be as shown in the following table.

Example No.	Additive	Corrosion Rate in Mils Per Year			
		Steel	Aluminum	Copper	Brass
1	Blank (no treatment)	15.0	11.0	2.0	3.0
2	Zn <sup>++</sup> , 10 ppm	15.3	3.2	1.6	1.4
3	Benzotriazole, 10 ppm	24.5	5.3	0.3	0.2
4	Hydroxyethylidene diphosphonic acid, 10 ppm	11.1	7.7	0.7	2.2
5	Zn <sup>++</sup> , 10 ppm hydroxyethylidene diphosphonic acid, 10 ppm	8.4	5.4	2.2	2.6
6	Benzotriazole, 10 ppm, hydroxyethylidene diphosphonic acid, 10 ppm	5.7	4.0	0.2	0.2
7	Zn <sup>++</sup> , 10 ppm benzotriazole, 10 ppm hydroxyethylidene diphosphonic acid, 10 ppm	2.0	0.2	0.2	0.3

As shown in the above table, Examples 5, 6 and 7 corresponding to the compositions of this process provide a corrosion protection far greater than would be expected in view of

the effects of the individual components thereof.

### Zinc and Polymaleic Anhydride

A. Harris, J. Burrows and T. I. Jones; U.S. Patent 3,897,209; July 29, 1975; assigned to Ciba-Geigy Corporation describe a method for inhibiting the corrosion and scale forming tendencies of water or an aqueous system which comprises treating the water or aqueous system with from 0.1 to 500 ppm of an additive combination comprising zinc and hydrolyzed polymaleic anhydride.

*Examples 1 through 13:* Some laboratory corrosion tests were carried out to show the synergistic effect of combining hydrolyzed polymaleic anhydride and zinc, and to show that hydrolyzed polymaleic anhydride is the only common polycarboxylic acid which gives this synergistic effect. The test method is referred to as the Aerated Solution Bottle Test. In each of these tests, and in the Laboratory Heat Exchanger Rig Tests to be subsequently described, the hydrolyzed polymaleic anhydride was prepared as follows.

250 parts of maleic anhydride were dissolved in 500 parts of toluene by heating to 70°C. To this solution was added a solution of 71.5 parts benzoyl peroxide (70% paste in dimethylphthalate) in 250 parts of toluene over 30 minutes. The solution was heated to 90°C and maintained there for 5 hours; during this time the polymer precipitated from the solution. Some of this polymer was isolated and found to have a molecular weight of approximately 470 by osmosis.

150 parts of water were added slowly at 60°C to the solution/precipitated polymer and the mixture stirred for 1 hour. On stopping the stirrer, a separation of the mixture into two layers was obtained. The upper toluene layer was removed and the aqueous solution was stripped under reduced pressure, to remove traces of toluene. The product was a brown colored solution of hydrolyzed polymaleic anhydride with a solids content of about 70% by weight, the polymer having a calculated molecular weight of 560. To carry out the Aerated Solution Bottle Test, a standard corrosive water is made up from: 20 grams of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 15 grams  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 4.6 grams  $\text{NaHCO}_3$ , 7.7 grams  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , and 45 gallons distilled water.

Mild steel coupons, 5 cm x 2.5 cm are scrubbed with pumice, immersed for 1 minute in hydrochloric acid and then rinsed, dried and weighed. The desired proportion of additive combination is dissolved in 100 ml of standard corrosive water, a steel coupon is suspended in the solution, and the whole is stored in a bottle in a thermostated water bath at 22°C. During the storage period, air is passed into the solution at 500 ml/min, the passage of the air being screened from the steel coupon; any water losses by evaporation are replaced as they occur with distilled water from a constant head apparatus.

After 48 hours, the steel coupon is removed, scrubbed with pumice, immersed for 1 minute in hydrochloric acid inhibited with 1% by weight of hexamine and then rinsed, dried and reweighed. A certain loss in weight will have occurred. The test results are expressed as a weight loss in milligrams, and are given in the following table. In each case,  $\text{Zn}^{++}$  was added as zinc nitrate hexahydrate, and the polyacrylic acid, and polymethacrylic acid had molecular weights respectively of 20,000 and 15,000.

Test Results at 100 ppm of Additive Combination Compared with a Blank

Ex. ample	RELATIVE PROPORTIONS		WEIGHT LOSS IN MILLIGRAMS WITH SPECIFIED POLYCARBOXYLIC ACID		
	Zinc	Poly- carboxylic acid	Poly- acrylic acid	Polymeth- acrylic acid	Hydrolyzed polymaleic anhydride
—	0	0	99.0	99.0	99.0
—	100	0	66.5	66.5	66.5
—	90	10	51.5	62.0	33.0
1	80	20	50.0	61.5	17.4
2	75	25	—	—	—

(continued)

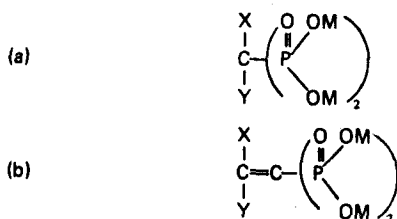


## Corrosion Inhibitors

Ex- ample	RELATIVE PROPORTIONS		WEIGHT LOSS IN MILLIGRAMS WITH SPECIFIED POLYCARBOXYLIC ACID			
	Zinc	Poly- carboxylic acid	Poly- acrylic acid	Polymeth- acrylic acid	Hydrolysed polymaleic anhydride	
3	70	30	48.0	56.5	4.2	
4	60	40	56.5	50.0	3.0	
5	50	50	54.5	50.5	2.0	
6	40	60	39.0	59.0	3.6	
7	30	70	59.0	56.0	6.0	
8	25	75	—	—	7.5	
9	20	80	60.0	56.0	4.8	
10	15	85	—	—	4.0	
11	10	90	55.5	56.5	6.0	
12	5	95	—	—	19.5	
13	2.5	97.5	—	—	20.0	
—	0	100	58.0	57.0	32.0	

## Organophosphorus Ligand-Divalent Zinc Complex

W.A. Feiler, Jr.; U.S. Patent 3,738,806; June 12, 1973; assigned to Monsanto Company describes a method of inhibiting the corrosion of ferrous metals and nonferrous metals in contact with an aqueous corrosive medium. The process comprises maintaining in the medium a complex formed by (1) an organophosphorus ligand selected from the group consisting of:



(c) and mixtures thereof, where X and Y each are hydrogen, hydroxyl, lower alkyl group containing 1 to 4 carbons, or lower alkenyl group containing 2 to 4 carbons, and M is hydrogen, ammonium, alkali metal or lower alkyl amine and (2) a metal ion which includes zinc, nickel, cobalt, cerium, lead, tin, calcium, ferrous, ferric, chromium, chromic, mercurous, mercuric, or manganese. An example is a complex formed by the divalent ion zinc, and the ligand 1-hydroxy-1,1-ethylidene diphosphonic acid.

## Zinc Cations, Benzotriazole and Sulfuric Acid

C. O'Neal, Jr., and J.A. Goetz; U.S. Patent 3,794,603; February 26, 1974; assigned to The Sherwin-Williams Company describe corrosion-inhibiting compositions of  $Zn^{++}$  cations, benzotriazole and  $H_2SO_4$ , alone or in combination with other corrosion-inhibitors. Addition of diethylenetriaminepentaacetic acid allows formulation of a corrosion-inhibiting composition having a neutral pH. The following examples illustrate the process. The terms percent and parts refer to percent and parts by weight, unless otherwise indicated. The term BT means benzotriazole. (H) BT refers to the hydrogen form of benzotriazole, which is a weak acid, as distinguished from, for example, the sodium salt.

**Example 1:** A  $Zn^{++}$ -BT- $H_2SO_4$  corrosion-inhibiting solution was prepared as described below. A 4 ml portion of  $H_2SO_4$  (16%) was added to 35 ml  $ZnSO_4$  (20%). After mixing, a 35 ml portion of sodium BT was added to the  $Zn^{++}$ - $H_2SO_4$  solution. No precipitate formed. The corrosion-inhibiting solution contained 4.25% by weight  $Zn^{++}$  cations, 1.81% by weight (H) BT, and 0.86% by weight  $H_2SO_4$ , balance water.

The effectiveness of the  $Zn^{++}$ -BT- $H_2SO_4$  solution was tested by means of an  $H_2S$  corrosion chamber. Two copper specimens were thoroughly cleaned; one specimen was dipped in the