# Benzotriazole: An effective corrosion inhibitor for copper alloys

Copper is the only engineering metal that is noble metal. It resists many corrosive environments. But copper tarnish or corrodes under some circumstances.

In recent years, investigators have shown that a system of tarnish or corrosion control for copper, brass and bronze can be built around the organic compound, 1, 2, 3, benzotriazole.

Benzotriazole forms a strongly bonded chemisorbed two-dimensional barrier film less than 50 angstroms thick. This insoluble film, which may be a monomolecular layer, protects copper and its alloys in aqueous media, various atmospheres, lubricants, and hydraulic fluids. Benzotriazole also forms insoluble precipitates with copper ions in solution (that is, it chelates these ion), thereby preventing the corrosion of aluminum and steel in other parts of a water system.

J. B. Cotton. Imperial Metal Industries Ltd., Birmingham, England, has studied the tarnishing of copper and copper alloys exposed to humid environments, and the possibility of the prevention of staining by reaction with triazole type compounds. At the Second International Congress on Metal Corrosion, New York, 1963, he summarized the properties of commercially available benzotriazole and the reaction of this class of compound with copper ions. His report, “Control of Surface Reaction on Copper by Means of Organic Reagents”, points out that the nitrogen-hydrogen group, and at least one of the other nitrogens in the ring, is involved in the complex bonding arrangements to copper. The polymeric chains or monomolecular plate-like complexes completely cover a clean metal surface, affording excellent protection. In the more typical case, benzotriazole probably plugs holes and defects in the copper oxide surfaces film.

Use of benzotriazole, and other protective chemicals such as tolutriazole, constitutes a significant advance in the quest for corrosion inhibitors. It demonstrates that effective inhibition can function through the formation of true chemical bonds.

The compound can also control the reaction between copper or copper alloy surfaces and typical environments. It is a useful additive to antifreeze and other water circulating systems; it can be incorporated into lacquers, protective wrapping papers, lubricants, hydraulic fluids, and alkaline detergents.

This data sheet reviews the literature and patents on the use of benzotriazole as a tarnish and corrosion inhibitor for copper and copper alloys it covers literature on the subject since 1957 in six application areas: Lacquers, Varnishes and Insulation, Storage and Packing, Lubricants and Sealants, Electrolytic Processes, Cleaning Solutions, and Water Systems.

## Laquers, Varnishes, and Insulation

The natural color copper, its alloys and colored finishes applied by chemical treatment can be protected by a transparent lacquer inhibited with benzotriazole. Incralac, a finish developed by the copper industry, is an example. It is a trans-

parent lacquer which was developed as a result of research sponsored by the International Copper Research Association. Intended primarily for use on outdoor architectural metal work, it preserves the natural colors of copper and its alloys for long periods (1.2) it can also be used on copper and its alloys indoors.

Incralac contains an acrylic ester resin dissolved in a solvent such as toluene. Benzotriazole is added as a corrosion inhibitor, and epoxidized soya bean oil as a leveling agent. Incralac-coated test panels exposed in London and on the South Coast of England have remained untarnished for several years.

The inhibitor effectively combats tarnish beneath lacquer films. This mode of failure is due primarily to peroxides formed during the early stages of degradation Of the lacquer film and residual solvent under the influence of ultraviolet radiation. (3) Greatly increased protection is afforded by the incorporation of suitable ultraviolet absorbers, antioxidants and copper complexing agents. Careful cleaning and spraying are essential. (4) Wiping with an inhibitor-cleaner (40 grams benzotriazole in a gallon of water) is recommended as the last cleaning step before the coating is applied. (5)

Benzotriazole has also proved beneficial in paints, pigmented lacquers and inks.(6) Example a bronze lacquer, containing 4g of bronze pigment powder and 100 g of cellulose nitrate clear lacquer (30% solids), was dived and to one portion was added 1% benzotriazole. After aging for 3 days, the untreated fraction had turned dark green, but the treated fraction had not changed.

In another application, the tendency of polypylene electrical insulation to oxidize more rapidly in the presence of copper is corrected by adding an antioxidant and benzotriazole to the insulation.(7)

The role of benzotriazole in preventing copper staining has been studied by making polarization curves in 3% sodium chloride under potentiostatic control. (8) Significant differences in cathodic behavior have been found in treated and untreated samples with smaller but reproducible differences in anodic behavior. Unsuccessful coating treatments gave polarization curves similar to those observed untreated samples. Benzotriazole suppresses the cathodic reduction of oxygen but does not appear to affect hydrogen discharge. Thus, to some extent it functions as a cathodic inhibitor, but it also serves more significantly as an anodic inhibitor.

(1) Incralac Protection for Copper, Metal industry (London), 104, 696-697(1964).

(2) Surface Finishes for Copper and Copper Alloys, N. R. Bharucha, Symposium on Copper in Modern Buildings, Copper Development Association (London), pp. 17-22, 96-98(1965).

(3) Clear Lacquers for Copper and Copper ALLOYS, n. r. Bharucha and M. T. Baker, Summary of Research Carried Out by British Non-Ferrous Metals Research Association for International Copper Research Association, Inc., New York. 20 pp. (1965)

(4) Incralac Progress, A. P.C. Hallowes, Copper, (28) 19-21 (Summer 1966).

(5) Incralac – Protective Coating System for Copper metals in Exterior Service. International Copper Research Association, Inc., New York. 5 pp. (1968).

(6) Inhibiting Copper Corrosion, J. K. Aiken, D. K. Howard, and A. F. Popplewell, Geigy Company Ltd., British Patent 994,409 (June 10, 1965)

(7) Benzotriazoles…as Inhibitors for Oxidation of Polypropylene Electrical Insulation in the Presence of Copper, R. H. Hansen, Bell Telephone Laboratories, Inc., U.S. Patent 3,367,907 (February 6, 1968)

(8) An Electrochemical Investigation on the Prevention of Staining of Copper by Benzotriazole, I. Dugdale and J. B. Cotton, Corrosion Sci., 3 (2), 69-74 (1963)

## Storage and Packing

Finished parts, mill products, and powders of copper, brass and bronze can be protected from tarnishing during storage and shipping if they are wrapped in material inhibited with benzotriazole or are coated with a film of the inhibitor. Benzotriazole also can be incorporated into protective waxes or pasts to impart a tarnish-resistant film.

The compound has been deposited on cold metal from a vapor at 85 C. (1) The simplest way is to dip the metal part in a 0.25% aqueous solution of benzotriazole at 60 C for 2 min. Brass strip may be run continuously through such a solution. (2) Packing material may be treated by soaking it in a solution containing 0.1 to 5% and 1%. (3,4)

Benzotriazole treated papers interleaved between sheets of copper or copper alloy stacked in packing cases protect the metal from staining and discoloring for long periods. (5) Reels of copper wire can be protected by wrapping the outside with treated paper. (2) And copper items in sealed drums will not tarnish if the interiors are lined with impregnated paper.

Internal surfaces of waveguides and other microwave components can be protected by filling the bores with the shredded paper. Self-adhesive papers and vinyl tapes guard against scuffing and scratching during fabrication, storage and transit. The tapes are widely used in the printed circuit industry.

An abrasive-free wax or polish containing 0.1 to 10% benzotriazole inhibits staining of polished copper and copper-base alloy by washing solutions. The wax also slows tarnishing in the atmosphere. (6,7)

The benzotriazole may be added to the polish as a solution in a compatible solvent, or it may be dissolved in molten wax. Wax polish composed of 71% (by wt) white sprit, 13% carnauba, 7% paraffin, 5% benzotriazole, mixed 2 hours at 120 F, has protected polished copper from staining for 24 hours in a 0.25% salt solution mist. Unprotected articles were badly stained.

Dipping copper and copper alloys into a solution or dispersion of soluble ferricyanides and a benzotriazole derivative for 0.5 to 30 minutes arrests corrosion and tarnishing. (8,9) About 0.001 to 5% (by wt) of ammonium or alkali metal ferricyanides or a mixture or several of these salts has been used with 0.01 to 0.5% benzotriazole. Alkali metal salts would be preferable to avoid stress corrosion cracking which may occur in stressed parts in the presence of ammonia.

The benefits of the films have been measured by exposing sheets to corrosive atmospheres. For example, when dipped into an aqueous solution of 0.1% benzotriazole derivative and 0.05% $K_3Fe(CN)_6$ at 65 F for 2 minutes, a clean copper sheet will not tarnish if exposed for 2 hour in an atmosphere containing 10 ppm hydrogen sulfide. But tarnish appears in 2 minutes on sheets dipped in a solution containing only potassium ferricyanides (0.05%), and it appears in 20 minutes when the sheet is immersed in one with only benzotriazole (2%).

Another method of improving tarnish resistance is to first apply a soap solution or chromate solution followed by treatment with a benzotriazole solution. (10)

Treatment with benzotriazole can be incorporated into the production of sheet from copper and copper alloy powders. (11) The method includes there steps: (1) compacted standard electrolytic copper powder by passing it through a pair of rolls; (2) sinter at 1000 F in a hydrogen atmosphere for 15 minutes to get oxide-free sheet with 25% porosity; (3) immerse the sheet in a 5% aqueous solution of benzotriazole at 100 F, allowing the solution to cool to 60 F over a period of 8 minutes, then holding at 60 F for 2 minutes; (4) dry the sheet in air; (5) compact it further by cold rolling it 50% Untreated stock stained within 18 hours in a polluted atmosphere; treated sheet remained unstained for 30 days.

Tarnishing of copper articles such as plumbing fixtures during storage can be prevented by treatment with a benzotriazole solution. Solderability is also improved.

Also, stressed brass parts apparently do not fail by stress corrosion in an atmosphere contaminated with sulfur dioxide if the parts are protected with benzotriazole. The film will not prevent cracking in an ammonia atmosphere. (2)

(1) Improvements in or Relating to Corrosion Inhibitors for Copper and Copper-Containing Alloys, Imperial Chemical Industries Ltd., British Patent 907,793 (October 10, 1962)

(2) Benzotriazole and Related Compounds as Corrosion Inhibitors for Copper, J. B. Cotton and I. R. Scholes, Brit. Corros. J., 2 (1), 1-5 (1967)

(3) Improvements in or Relating to the Inhibition of Corrosion of Copper and Copper and Copper-Containing Alloys, Imperial Chemical Industries Ltd., British Patent 907,794 (October 10, 1962)

(4) Vapor Phase Corrosion Inhibitor for Copper and Copper Alloys, J. B. Cotton, Imperial Chemical Industries Ltd., German Patents 1,186,503 (November 26, 1964) and 1,186,725 (February 4, 1965).

(5) Brighter Outlook, A. P. C. Hallowes, Copper, (15) 4-6 (Summer 1962).

(6) Corrosion Inhibitors for Copper and Its Alloys, J. B. Cotton, Imperial Chemical Industries Ltd., British Patent 947,115 (May 6, 1964).

(7) Non-Oxidizing, Tarnish-Preventing Metal Cleaning Pastes, J. R. Geigy AG, Belgian Patent 656,693 (June 4, 1965).

(8) Corrosion Inhibitor for Copper and Its Alloys, J. R. Geigy AG, Brigian Patent 658,763 (July 26, 1965).

(9) Treatment of Metal Surfaces to Inhibit Tarnishing or Corrosion Thereof, D. K. Howard and A. F. Popplewell, Geigy (U.K.) Ltd., British Patent 1,069,391 (May 17, 1967).

(10) Corrosion Preventing Treatment, D. K. Howard and A. F. Popplewell, Geigy (U.K.) Ltd., British Patent 1,065,997 (April 19,1967).

(11) Inhibition of Corrosion of Copper, J. B. Cotton, Imperial Metal Industries (Kynoch) Ltd., British Patent 1,031,503 (June 2, 1966).

### Lubricants and Sealants

Copper is almost always resistant to mineral oil lubricants, but it may stimulate the deterioration of them. When acidic products form, they can corrode steel and copper. Lubricants containing sulfur may discolor copper. However, addition of benzotriazole to lubricants and sealants greatly slows or prevents corrosion.

A lubricating-oil compound has been formulated of ester-base oil and 0.2 to 2% alkylated benzotriazole. (1) Organosiloxane greases which are used as lubricants, dielectrics, and sealing compounds become less corrosive to copper and steel when 0.02 to 0.06% benzotriazole is added. (2) The grease has prevented corrosion of copper strips immersed in distilled water at 70 F for 4 weeks. The inhibitor is also effective in hydraulic fluids. (3)

(1) Rust Inhibitors for Lubricating Oils, R. T. Davies, M. F. Hoare, and H. G. Krischai, Esso Research and Engineering Company, British Patent 793,115 (April 9, 1958).

(2) Organosiloxane Greases, Midland Silicones Ltd., British Patent 809,831 (March 4, 1959).

(3) Hydraulic Fluids, Joseph Lucas Industries Ltd., British Patent 867,181 (1961).

### Electrolytic Processes

Benzotriazole had been suggested as a parting agent which helps separate cathode deposits from starting sheets or master forms in electrolytic refining and electroforming. There is evidence that benzotriazole codeposits with copper from a plating solution. Its effect on electrodeposits has been studied by assign it to copper sulfate plating solutions. (1)

Benzotriazole in acid copper sulfate solutions form an insoluble cuprous complex which codeposits with copper. (2) Additions of 0.012 g per liter gives fine-grained deposits of copper and prevents epitaxy; 0.12 g per liter gives fully bright deposits with a banded structure. There are reports, however, that soluble copper will precipitate benzotriazole, thus ending its beneficial effect.

Other research suggests that the benzotriazole may be detrimental. It may result in residual stress in the deposit which causes cracking and lack of adherence. (3,4) No improvement in corrosion resistance was observed during this work.

Use of 0.1 to 1.0% aqueous solutions of benzotriazole to aid in stripping copper sheets, foils, starting sheets, and electroformed articles from copper cathodes had been proposed, (5) but in practice it has had little effect.

Adding 5 to 10% (by wt) alcohol as a wetting agent to the benzotriazole solution insures uniform coverage of the cathode surface. If perfected, the method would be useful in the continuous production of copper sheet by electrodeposition on a copper drum. The benzotriazole solution would be applied before the revolving drum re-enters the electrolyte.

(1) Effect of Codeposited Material on the Corrosion Behavior of Electrodeposits, J. K. Prall and L. L. Shreir, Corrosion Sci., 1,181-182 (1961)

(2) Benzotriazole as an Addition Agent for Acid Copper Solution, J. K. Prall and L. L. Shreir, Trans. Inst. Metal Finishing, 41 (1), 29-30 (1964)

(3) Corrosion Resistance of Electroplated Copper with Codeposited Benzotriazole, M. G. Kendall, Final Report to International Copper Research Association, Inc., New York, 28 pp. (1966).

(4) Stress in Copper Electrodeposits made with Benzotriazole as Addition Agent, R. Walker, Electrochim Acta 10 (7), 1861-1866 (1968).

(5) Stripping Electrodeposited Materials from the Cathode, Anaconda American Brass Co., British Patent 993,392 (May 26, 1965).

## Cleaning Solutions

Copper articles will not tarnish when washed with detergent solutions if the solutions contain small amounts of benzotriazole. Only a few parts per million benzotriazole are needed in detergents containing wetting agents and calcium sequestering polyphosphates. (1,2,3) Benzotriazole is among several compounds which prevent discoloration of copper, brass, and copper-nickel-zinc alloys (nickel silver) by aqueous solutions of (1) detergents whish are high-molecular-weight organic sulfonation products, (2) certain inorganic slats, such as polyphosphates, sodium sulfate, and sodium chloride, and (3) combinations of (1) and (2). About 0.01% of the inhibitor is all that is necessary to be effective.

Dry cleaning fluids containing detergents often are corrosive to copper and other metals. About 50 ppm of benzotriazole in the fluid will prevent attack on copper and iron. (4)

Scoured surfaces of copper and copper alloys can be protected against corrosion when in contact with water (particularly with aqueous alkaline solutions) if about 0.1% (by wt) of 2-guanidino-aryloimidazole compounds (derivatives of benzotriazole) are added to the water or to the solutions. (5)

(1) Detergent Compositions Containing Metal Discoloration Inhibitors, J. R. Schaeffer, Procter & Gamble Co., U.S. Patents 2,618,606 and 2,618,608 (November 18, 1952).

(2) Composition for Inhibiting Metal Tarnish, J. R. Schaeffer, Procter & Gamble Co., Canadian Patent 522,940 (March 20, 1956).

(3) Compositions for Inhibiting Metal Tarnish, Procter & Gamble Co., British patent 652,339 (April, 1951).

(4) Noncorrosive Dry Cleaning Compositions, S. G. Levy, D. A. Baker and R. F. Monroe, Dow Chemical Co., U.S. Patent 3,337,471 (August 22, 1967).

(5) Process for the Protection of Copper and Alloys Thereof, and Corrosion Inhibiting Compositions, J. R. Geigy Co. Ltd., British Patent 782,039 (August 28, 1957).

## Water Systems

Sodium mercaptobenzotriazole is often added as a corrosion inhibitor in recirculating water for engine cooling, air conditioning, heating systems, and industrial equipment containing copper components. Recently, benzotriazole has been found to be effective in a variety of such aqueous environments. It is often used with borates in antifreeze, and in certain cases it will protect copper tubing from pitting corrosion by an otherwise aggressive water. Since the inhibitor does not break down below about 350 F, it can control corrosion of copper effectively in hot water in a mixed metal system.

Antifreezes have been proposed with consist of water-soluble alcohols as the chief nonaqueous ingredients plus anticorrosion agents containing 0.4 to 80% benzotriazole, its ammonium salt, or tetrabortate, or their mixtures. (1) The amount of the agent in the antifreeze is sufficient to produce a concentration of about 0.01 to 2.0% benzotriazole or its salt and 0.5 to 3.0% of the weight of the water soluble alcohols.

Another antifreeze consists of a water-soluble alcohol, particularly ethylene glycol, and an agent containing 0.2 to 77% benzotriazole, its alkali metal or ammonium salt or their mixtures, or N-alkylbenzotriazole; 2.2 to 80% of an alkali metal arsenite, arsenate or molybdate or their mixtures; and 11 to 96% of a material which maintains the pH of the aqueous solution of the anticorrosion agent at about 7.5 to 10.5. The anticorrosion agent is present in an amount sufficient to produce concentrations of 0.01 to 2.0% benzotriazole; 0.1 to 2.0% arsenite, arsenate, or molybdate; and 0.5 t 2.5% of the buffer.

Other corrosion inhibitors for ethylene glycol solutions have been proposed. For example, one contains 1 part phosphoric acid (density 1.75) and sufficient technical triethanolamine (usually about 3 parts by wt) added to 100 parts ethylene glycol to bring the pH of a 50% aqueous solution of the mixture to 7.2. The resulting composition shows less tendency to corrode metals than a corresponding composition in which the benzotriazole is replaced by 0.2 to 0.3 parts sodium mercaptobenzotriazole.

Similarly, excellent corrosion inhibition is obtained by use of 0.35 to 3.0 parts (by wt) of phosphoric acid, 0.05 to 1.0 parts of benzotriazole and 0.05 to 0.50 parts of cyclohexylamine or by use of a mixture containing 0.5 parts of sodium nitrate, 0.1 to 1.0 parts benzotriazole, and 0.2 to 3.0 parts cyclohexylamine. All of these compositions, when diluted with four volumes of water, are suitable for engine cooling. They have freezing points below 0 F.

It is also claimed that an antifreeze containing 3 to 15% benzotriazole is especially useful in preventing cavitation corrosion in high speed coolant pumps having aluminum housing and impellers. (3). This could aid service life.

Antifreeze compositions appear suitable as additions to exchange liquids in heat exchange systems. (4) These are stable solutions which include a water-

soluble solution condensation product of an aminoalkyl silicate and an oxirane grouping, in a water-immiscible organic liquid. One of the proposed compositions contains either 1% (by wt) benzotriazole or sodium mercaptobenzotriazole.

Corrosion in hot water can be prevented by adding mixture of 1 to 2% triethanolammonium phosphate and 0.01 to 0.2% benzotriazole (or mercaptobenzotriazole) at pH 7.5 to 9.0. (5) Also, solutions of 1,2,3-triazole are effective corrosion inhibitors for plumbing containing iron and copper parts. (6) Aerated tap water containing 0.1% of a 3-to-1 mixture of sodium nitrate and sodium borate causes one hundredth as much corrosion of steel in the presence of cooper when benzotriazole (1% of the weight of the mixture) is added. The inhibitor action of benzotriazole (5 mg per liter) is greatly increased by the presence of 50 mg per liter of highly condensed polyphosphates ($P_20_5$:$Na_20$ 1:1-1.5).

Domestic hot water tanks made of copper have been treated with benzotriazole to inhibit pitting in certain corrosive waters. (7)

Corrosion in plumbing constructed of ferrous and non-ferrous metals is slowed if the aqueous solutions contain sodium nitrate, sodium borate and benzotriazole.(8) A synergistic effect results from the combination. The additive consists of about 75% sodium nitrate, 25% sodium borate and 1% benzotriazole and is used in a concentration of 1000 to 2000 ppm, Substitution of 1% mercaptobenzotriazole, KSCN diethyldithiocarbamate, 2-methylthiozole, 3-aminothiotriazole and s-trithiane for benzotriazole has proven less affective.

Inhibitors consisting of sodium nitrate (at least 0.02% sodium nitrite (at least 0.03%), sodium silicate (at least 0.05%) or cyanate or urea (at least0.10%), and sodium mercaptobenzothiazole or benzotriazole (at least 0.0125%) in water have been examined to determine their effect on corrosion of solder (70-30 lead-tin), aluminum, cast iron, mild steel, and copper. (9)

Also, 1 to 5 ppm 1,2,3-benzotriazole in recirculating water, with or without molecularly dehydrated phosphates, slows the corrosion of copper or copper alloys which are attached to more anodic metals such as iron, zinc, aluminum, or their alloys. (10). The compound is stable and effective in water treated with Chloramine-T for slime and bacteria control. The phosphate compounds may be Calgon-brand sodium phosphate glass, or a sodium-zinc phosphate glass having the molar composition 1.25 $Na_2O$.0.29 ZnO.$P_2O_5$, in amounts of 25 to 50 ppm.

Benzotriazole additions to water have been effective in preventing galvanic corrosion in mixed metal systems such as copper-steel, copper-zinc, and copper-aluminum.(11) In experiments on aluminum-copper and aluminum-copper-iron couples in domestic water, benzotriazole inhibits corrosion of aluminum-copper couples and 2-benzimidazolethiol aluminum-copper-iron couples. Tests on aluminum-copper couples in natural sea water showed that 2, 5-dimercaptothiadiazole reduced corrosion of the aluminum electrode. (12)

The benefits of benzotriazole as an inhibitor of copper corrosion have been observed in closed-circuit water-cooled stators. (13) The initial does should leave a film on the copper and bring the benzotriazole concentration in the water up to about 20 to 100 ppm. This concentration should be maintained by periodic benzotriazole additions.

In the presence of radiation, benzotriazole is an effective inhibitor of copper corrosion by reactor cooling water. (14)

Russian investigators have studied the effect of different concentrations of benzotriazole on the rate of corrosion of steel and copper at 17 F. (15) In tests

lasting 60 to 90 days, 0.001% benzotriazole completely protected copper. Corrosion of gray cast iron was reduced 8 to 10 times by 1% benzotriazole. In a 0.1% buffer solution containing benzotriazole and its sodium salt at a pH of 7.3 to 7.5, the corrosion rate for gray cast iron and for steel were the same as in a solution containing 1% benzotriazole at a pH of 5.9 to 6.2. The buffer solution was the most effective. Concentrations of 0.5% eliminated corrosion of gray cast iron; 0.2% solutions protected steel; 0.6% protected steel in contact with copper and 0.001% protected copper.

In other work on the protective properties of benzotriazole with respect to the corrosion of copper and steel in neutral and acid solutions, it was concluded that despite a certain inhibiting action, benzotriazole could not be considered an effective anticorrosive agent for ferrous metals in neutral media. (16) It proved effective, however, in preventing the corrosion of copper by itself and in contact with steel. In acid media, benzotriazole prevented the corrosion of copper, but visible compounds formed on the surface on the metal. For acid solutions a related compound, 25-dimercaptothiadiazole, seems to be a better inhibitor than benzotriazole. (17) Benzotriazole is effective in reducing attack on copper by 3% sodium hydroxide and 0.5 N sodium hydroxide plus 1.0 N ammonium sulfate. (18)

In steam condensate systems of mixed construction, amines are used to control steel corrosion but they will accelerate copper attack by forming complexes. When benzotriazole is added, copper corrosion can also be prevented. (19)

(1) Antifreeze Compositions, A. D. Meighen, Commercial Solvents Corp, U.S Patents 2,803,603 and 2,803,604 (August 20, 1957)

(2) Ethylene Glycol Antifreeze Solutions, J. D. Kendall, D. J. Fry, and B. A. Lea, Ilford Ltd., British Patent 811,675 (April 8, 1959).

(3) Antifreeze Composition, R. F. Monroe and A. J. Maciejenske, Dow Chemical Co.,U.S. Patent 3,291,741 (December 13, 1966).

(4) Improvements in or Relating to the Inhibition of Corrosion of Metals, Holt Products Ltd., British Patent 1,007,927 (October 22, 1965).

(5) Inhibitor for Hot-Water Corrosion in Boilers, E. Krietch, German Patent 1,111,900 (Appl. September 20, 1958).

(6) Inhibiting the Corrosion of Pipe Systems Made of Iron and Copper or their Alloys, R. W. Liddell and G. Birdeye, Chemische Fabrik Joh. A. Benckiser GmbH., German Patent 1,046,438 (December 11, 1958).

(7) Benzotriazole and Related Compounds as Corrosion Inhibitors for Copper, J. B. Cotton and I. R. Scholes, Brit. Corros. J., 2 (1), 1-5 (1967).

(8) Benzotriazole-Containing Corrosion Inhibitors for Ferrous Metals, R. W. Liddell, Hagan Chemicals & Controls, Inc., U.S. Patent 2,877,188 9March 10, 1959).

(9) Composition for Inhibiting Corrosion of Metals in Aqueous Systems, Imperial Chemical Industries Ltd., British Patent 1,001,222 (August 11, 1965).

(10) Corrosion Inhibitors for Copper with Water, G. B. Hatch, Hagan Chemicals & Controls, Inc., U.S. Patent 2,942,953 (June 21, 1960).

(11) Corrosion Inhibitors, Albright & Wilson (Mfg.) Ltd., British Patent 865,192 (April 12, 1961).

(12) Organic Inhibitors for Copper, M. G. Burberry and G. L. Greenfield, Final Report to International Copper Research Association, Inc., New York. 34 pp. (1968).

(13) Corrosion Control in a Water-cooled Stator, K. H. Wall and I. Davies, j. Appl. Chem., 15 (8), 389-392 (1965).

(14) Radiolytic Corrosion and Related Problems in the Cooling Water Circuits of High-Energy Particle Accelerators, F. Hoyer, M. Bourges and R. Deltenre, CERN, Eur. Organ. Nucl. Res., CERN 68-2, 16 pp. (1968).

(15) Compounds of the Azole Group as Corrosion Inhibitors of Ferrous Metals and Copper, I. Protective Action of Benzotriazole in Neutral and Acid Solutions, T. G. Neznamova, V. P. Dobrovol'skaya, and V. P. Barannik, Zh. Prikl. Khim., 38 (10), 2388-2390 (1965).

(16) Protective Action of Benzotriazole in Neutral and Acid Solutions, T. G. Neznamova, V. P. Dobrovol'skaya, and V. P. Barannik, Ukrain. Fiz. Zhur., 31 (12), 1337-1341 (1965).

(17) New Organic Corrosion and Tarnishing Inhibitors for Copper, N. R. Bharucha, Report to International Copper Research Association, Inc., New York (1966).

(18) Inhibiting Action of Benzotriazole, Mercaptobenzothiazole…in Ammonia and in Caustic Soda in the Presence of Ammonium Ions, V. P. Dobrovol'skaya, T. G. Neznamova, and V. P. Barannik, Zh. Prokl. Khim., 40 (8), 1841-1843 (1967).

(19) Mutual Effects of Benzotriazole and Amines on Corrosion Prevention in Steel and Copper, S. A. Balezin, E. G. Zak and F. B. Glikina, Zashchita Metallov, 4 (1) 111-114 (1968).