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3,531,414

CORROSION-INHIBITING AGENTS

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No Drawing. Continuation-in-part of application Ser. No. 479,344, Aug. 12, 1965, now Patent No. 3,452,038. This application Oct. 25, 1968, Ser. No. 770,851
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Int. Cl. C11d 1/02, 3/28
U.S. Cl. 252—152 30 Claims

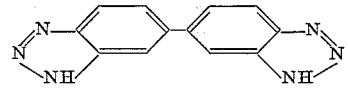
ABSTRACT OF THE DISCLOSURE

A process for treating metallic surfaces with bis-benzotriazoles in the molecules of which two benzotriazole moieties are linked by means of a direct carbon-to-carbon bond, or by a straight chain or branched alkylene, cycloalkyl, carbonyl, sulphonyl, oxygen or sulphur bridge, whereby tarnishing and corrosion of such surfaces are inhibited and compositions, among them functional materials, containing such bis-benzotriazoles and producing such inhibition or metallic surfaces, are described.

The present application is a continuation-in-part of our pending application, Ser. No. 479,344, filed Aug. 12, 1965, now Pat. No. 3,452,038.

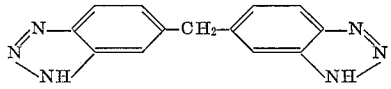
The present invention relates to processes of inhibiting the tarnishing or corrosion of metals or metal alloys and to processes of inhibiting metal-induced deterioration of functional materials, and in a further aspect to compositions comprising bis-benzotriazales for use in said processes.

According to a first aspect of the present invention, a process of treating a metal or metal alloy surface to inhibit tarnishing or corrosion thereof comprises contacting the metal or metal alloy surface with a bis-benzotriazole of the formula



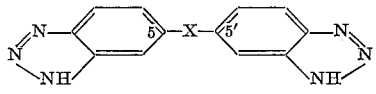
I

or with 5:5′-methylene-bis-benzotriazole, of the formula



II

or with a bis-benzotriazole compound of the formula



III

wherein X represents (a) a divalent straight chain alkylene bridging group containing from one to six carbon atoms in the chain and being substituted with from one or two alkyl groups containing each from one to four carbon atoms where the alkylene group contains only one carbon atom, or being unsubstituted or substituted with at least one alkyl group containing from one to four carbon atoms where the alkylene group contains two or more carbon atoms; (b) 1:1-cycloalkyl residue containing at least five, and preferably five or six carbon atoms; (c) a carbonyl group; (d) a sulfonyl group; or (f) a sulfur atom.

Preferably X, as defined under (a) and being alkyl-substituted, bears as substituents from one to four alkyl groups each containing from one to four carbon atoms.

In this specification and the appended claims, the term

"metallic surface" is used generically for both metal and metal alloy surfaces; "corrosion-inhibiting" is used generically for inhibiting corrosion as well as tarnishing.

If the bridging group X of Formula III represents an alkylene group, it contains from one to six carbon atoms; if one or more alkyl substituents are present in the alkylene group, the substituent may be a methyl, ethyl, n-propyl, iso-propyl, n-butyl or iso-butyl group. Examples of alkylene bridging groups X include ethylene, n-propylene, n-butylene, n-amylene, n-hexylene, methyl-methylene, dimethyl-methylene, ethyl-methylene, diethyl-methylene, propyl-methylene, dipropyl-methylene-, n-butyl-methylene, di-n-butyl-methylene, 1-methyl-ethylene, 1,2-dimethyl-ethylene, 1-ethyl-ethylene, 1,2-ethyl-ethylene, 1-n-propyl-ethylene, 1,2-n-propyl-ethylene, 1-n-butyl-ethylene, 1,2-n-butyl-ethylene, 1,1-dimethyl-ethylene, 1,1-diethyl-ethylene 1,1-di-n-propyl-ethylene, 1,1-di-n-butyl-ethylene, 1,1,2-trimethyl-ethylene or 1,1,2,2-tetramethyl-ethylene.

The process according to the invention is carried out in practice in a number of ways. Firstly the metallic surface can be treated with a solution containing one or several bis-benzotriazole compounds of Formulas I, II and/or III. A solution containing the bis-benzotriazole compound or compounds in a proportion in the range of from 0.001% by weight to saturation may be used, but a solution containing from 0.01% to 5%, and particularly containing from 0.1% to 1%, by weight of the bis-benzotriazole compound, calculated on the weight of the solution, is preferred. The bis-benzotriazole compounds of Formulas I, II and III are sparingly soluble in water or other aqueous media, and organic solvents, especially oxygenated hydrocarbon compounds, can be used, for example acetone and other dialkyl ketones, isopropanol and other alkanols, 2-methoxy-ethanol and other alkoxy-alkanols, or ethylene glycol or other alkylene- or dialkylene-glycols, depending on the nature of the bis-benzotriazole compound, the concentration desired and the mode of treatment of the metallic surface with the solution. Other organic solvents, for example, trichlorethylene, can also be used where appropriate.

The metallic surface may be treated with the solution in any convenient manner. For instance, the surface can be dipped into or passed through the solution containing the bis-benzotriazole compound. The surface can also be treated by padding with absorbent material soaked in the solution, or by spraying the surface with an atomized mist of the solution.

Other methods of carrying out the process according to the invention include condensing the vapor of one or several of the bis-benzotriazole compounds of Formulas I, II and/or III on the metallic surface; enclosing or otherwise wrapping the metal object bearing the surface to be protected in wrapping material impregnated with one or several of the bis-benzotriazole compounds of Formulas I, II and/or III; applying one or several of the said bis-benzotriazole compounds in an abrasive or non-abrasive polish composition to the metallic surface; and incorporating one or several of the said bis-benzotriazole compounds in other compositions, for example anti-freeze or coolant formulations, or in functional fluids, for example synthetic lubricants or polymeric formulations, which are normally applied to, or are used in the presence of, a metallic surface.

A first, preferred mode of carrying out the process of the invention in practice, comprises immersing the metallic surface to be protected in a solution of one or several bis-benzotriazole derivatives of Formulas I, II and/or III preferably containing from 0.01% to 5%, and optimally from 0.1% to 1.0% by weight of the said bis-benzotriazole derivatives, calculated on the total weight of the

solution, in a suitable solvent preferably at an elevated temperature, and most preferably a temperature within the range of from 60° to 100° C., and then allowing the treated metallic surface to dry in air or rinsing the surface with a suitable solvent to remove any surplus inhibitor solution and/or heating it to remove by evaporation any solvent remaining on the surface.

Another mode of carrying out the process of the invention in practice, comprises packing the surface of the metallic surface to be protected in wrapping material, for example, tissue paper impregnated with one or several bis-benzotriazole derivatives of Formulas I, II and/or III. The wrapping material may be impregnated by soaking in a solution containing from 0.1% up to 5% by weight of the said bis-benzotriazole derivative, calculated on the weight of the solution.

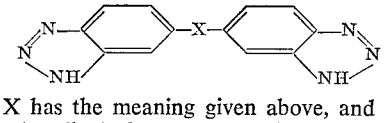
A third mode of carrying out the pocess of the invention comprises moving or suspending the surface of the metallic surface in an atmosphere saturated with the vapor of one or several bis-benzotriazole derivatives of the Formulas I, II and/or III so as to expose said surface to the action of said atmosphere. The vapor is conveniently maintained at 85° C. or a higher temperature, preferably a temperature within the range of from 100° C. to 160° C., and the metallic object may be chilled prior to being moved into the vapor to facilitate rapid condensation of the latter on the metallic surface to be protected.

A further mode of carrying out the process of the invention in practice comprises treating the surface of the metal with a non-abrasive wax or polish containing one or several bis-benzotriazole derivatives of Formulas I, II and/or III. The wax or polish preferably contains between 0.1% and 10% by weight of the said bis-benzotriazole derivative or derivatives. If solid wax is used, the bis-benzotriazole derivatives can be stirred into the molten wax and the mixture subsequently cast into a convenient form; if a liquid wax is used, the bis-benzotriazole derivatives can be added as a solution in a solvent which is compatible with the liquid base of the wax.

A fifth mode of carrying out the process of the invention in practice comprises treating the metallic surface with a suspension of an abrasive material suspended in a liquid or soft solid medium and containing one or several bis-benzotriazole derivatives of Formulas I, II and/or III. Preferably the amount of bis-benzotriazole derivatives in such suspension is within the range of from 0.01% to 5% and optimally within the range of from 0.1% to 1.0% by weight, calculated on the weight of the aforesaid medium.

The bis-benzotriazole derivatives of Formulas I, II and III possess useful corrosion-inhibiting properties when applied to metallic surfaces, particularly to surfaces of copper, copper alloys, cadmium, or cadmium alloys. The bis-benzotriazole derivatives of Formulas I, II and III can be used, for example, to inhibit corrosion of a metallic surface exposed to an atmosphere comprising sulfur dioxide, hydrogen sulfide or ammonia or other corrosive gaseous constituent; for example, brass or other copper alloys may be treated with a benzotriazole derivative or derivatives of Formulas I, II and/or III in accordance with the process of the invention, to inhibit stress corrosion cracking due to exposure to sulfur dioxide.

According to a second aspect of the present invention, there are provided bis-benzotriazoles of the formula



III

wherein X has the meaning given above, and which are useful as described above as corrosion-inhibiting agents.

The bis-benzotriazole derivatives of Formulas I, II and III can advantageously be used as, or be comprised in, corrosion-inhibiting agents for use in fluids in contact with copper or other metal surfaces, or as metal-protective ingredients in polishes or other compositions which can be applied to metallic surfaces to protect or improve the appearance of the surfaces. The said bis-benzotriazole derivatives are also valuable metal deactivators, particularly copper deactivators, when comprised in functional materials susceptible to deterioration of function in contact with the metal; such materials include functional fluids, and the said bis-benzotriazole derivatives when included in functional fluids for use at high temperatures, for example in high temperature synthetic lubricants.

According to a third aspect of the present invention, there are provided corrosion-inhibiting compositions for application to a metallic surface, and particularly to a copper or copper allow surface, containing, as corrosion-inhibiting agent a bis-benzotriazole derivative or derivatives of Formulas I, II and/or III.

The concentration of inhibitors in the corrosion-inhibiting compositions according to the invention is preferably within the range of from 0.01% to 5.0% and more preferably within the range of from 0.1% to 1.0% by weight based on the total weight of the composition, the concentration of the inhibitor varying according to the composition containing the inhibitor.

Typical compositions of the present invention include, for instance, abrasive and no-abrasive polish compositions, anti-freeze or coolant compositions and detergent compositions.

In the case of detergent compositions, of particular interest are detergent compositions comprising a water-soluble phosphate which acts as a sequestring agent for calcium ions and as corrosion-inhibiting agent a bis-benzotriazole derivative of Formula I, II and/or III and, optionally, water.

The water-soluble phosphate is preferably an alkali metal salt of a phosphoric acid which is poorer in water of constitution than orthophosphoric acid (H_3PO_4). Suitable phosphates include, for instance, sodium metaphosphate, potassium metaphosphate, disodium dihydrogen pyrophosphate, dipotassium dihydrogen pyrophosphate, tetra sodium pyrophosphate, tetrapotassium pyrophosphate, pentasodium triphosphate, pentapotassium triphosphate and mixed salts such as "hexasodium tetraphosphate" and "hexasodium hexametaphosphate."

In addition to the water-soluble phosphate and the bis-benzotriazole, the detergent compositions advantageously contain a surface-active agent. Although the surface-active agent may be, if desired, a nonionic surface-active agent, such as polyalkylene glycol derivatives of long-chain fatty amines, or a cationic surface-active agent for instance an alkyl pyridinium halide such as cetyl pyridinium bromide, it is particularly preferred to employ an anionic surface-active agent. Examples of preferred anionic surface-active agents include compounds having the formula

$$ROSO_3M \qquad IV$$

wherein R represents an aliphatic hydrocarbon group ad M represents an alkali metal or ammonium radical. The compound of Formula IV may be, for example, sodium myristyl sulphate, sodium hexadecyl sulphate, potassium stearyl sulphate, ammonium oleyl sulphate, sodium lauryl sulphate, potassium lauryl sulphate, ammonium or sodium stearyl sulphate and sodium oleyl sulphate. Other preferred classes of anionic surface-active agents include, for example, alkali metal alkyl benzene sulphonates such as sodium dodecyl benzene sulphonate and sodium dodecyl napththalene sulphonate; and alkali metal salts of secondary alkyl sulphates such as the sodium and potassium salts of 2-ethylhexyl sulphate.

The surface-active agent is preferably present in the detergent composition in a proportion of up to 40% by weight based on the total weight of the composition. More preferably, however, the surface-active agent is present in a proportion within the range of from 10% to 50% by weight based on the total weight of the composition.

The detergent compositions of the present invention are particularly valuable as detergent media for the cleaning of non-ferrous metals and alloys thereof and also glazed ceramics and the like. Household cutlery is often manufactured from nickel silver (sometimes called German silver) which consists of an alloy of zinc (17%), nickel (18%) and copper (65%). We have found that the compositions of the present invention provide excellent cleaning media for articles of cutlery made from this alloy, the said articles being substantially free from tarnishing or corrosion after the cleaning process.

Consequently, the detergent compositions of the present inventions should find wide application in the cleaning of houshold articles. In view of the low volatility of the compositions, giving rise to substantially no undesirable loss or small from hot washing solutions, together with the absence of attack on metal machine parts, the compositions of this invention are eminently suitable for use in mechanical dishwashing devices.

According to a fourth aspect, the present invention also provides a functional material per se susceptible to deterioration of function in contact with a metal, particularly copper or a copper alloy, which has been rendered less susceptible by comprising, as metal deactivator, a bis-benzotriazole derivative of Formulas I, II and/or III.

Typical functional materials include for instance synthetic lubricants based on carboxylic esters and functional oils such as cutting oils and transformer oils.

The concentration of inhibitors in the functional material is preferably within the range of from 0.0001% to 0.5% and more preferably within the range of from 0.001% to 0.01% by weight based on the total weight of the functional material.

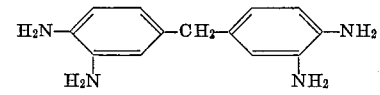
The compounds of Formulas I, II and III may also be advantageously used in metal or metal alloy protecting compositions or in functional materials in conjunction with other inhibitors, especially with inhibitors effective for the protection of ferrous metals.

Bis-benzotriazole, of Formula I, is produced by reacting 3:3':4:4'-tetraaminodiphenyl with nitrous acid or with a compound capable of forming nitrous acid under the conditions of the reaction, in the stoichiometric amounts required to diazotize only two of the four amino groups. The 3:3':4:4'-tetraaminodiphenyl may be treated, for example, with a mixture of an alkali metal nitrite and an inorganic acid. If desired, the reaction may be carried out under conditions similar to a conventional diazotization method, for example by treatment at a controlled temperature with an aqueous mixture of an alkali metal nitrite and hydrochloric acid, acetic acid or other inorganic or organic acid. The desired bis-triazole of Formula I is then formed by simultaneous elimination of two molecules of water under the diazotization conditions.

3:3':4:4'-tetraaminodiphenyl is produced, for instance, by reduction of 3:3'-dinitro-4:4'-diaminodiphenyl. The reduction can be carried out by treating the 3:3'-dinitro-4:4'-diaminodiphenyl with molecular hydrogen in the presence of a catalyst; the hydrogenation catalyst can be, for example, Raney nickel. The reduction can be carried out in practice by contacting 3:3'-dinitro-4:4'-diaminodiphenyl with a hydrogen-generating mixture, for instance with hydrochloric acid and iron or tin.

The 3:3'-dinitro-4:4'-diaminodiphenyl is, in turn, produced by nitration of 4:4'-diaminodiphenyl. The nitration is carried out by reaction with nitric acid by a conventional method. Preferably the amino groups of the 4:4'-diaminodiphenyl are protected during the nitration by conversion, for instance, into acetylamino or other acylamino groups. The conversion of the amino groups may be effected by reacting 4:4-diaminodiphenyl with the corresponding acid anhydride or acylhalide, and after the nitration has been carried out, the amino group can be regenerated by hydrolysis, for example, with an aqueous solution of an alkali metal hydroxide.

5:5'-methylene-bis-benzotriazole of Formula II is produced by reacting 3:3':4:4'-tetraaminodiphenylmethane of the formula



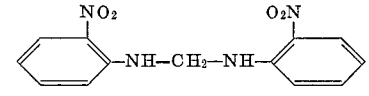
V

with nitrous acid or with a compound capable of forming nitrous acid under the conditions of the reaction in the stoichiometric amounts required to diazotize only two of the four amino groups. The 3:3':4:4'-tetraaminodiphenylmethane is treated, for example, with a mixture of an alkali metal nitrite and an inorganic or organic acid. If desired, the reaction is carried out under conditions similar to a conventional diazotization method, for example, by treatment at a controlled temperature with an aqueous mixture of an alkali metal nitrite and hydrochloric acid, acetic acid or other inorganic or organic acid. The desired 5:5'-methylene-bis-benzotriazole is then formed by simultaneous elimination of two molecules of water under diazotization conditions.

The 3:3':4:4'-tetraaminodiphenylmethane is produced for instance, by reduction of 3:3'-dinitro-4:4'-diaminodiphenylmethane. The reduction is carried out by treating the 3:3'-dinitro-4:4'-diaminodiphenylmethane with molecular hydrogen in the presence of a catalyst; the hydrogenation catalyst can be, for example, Raney nickel. The reduction is carried out in practice by contacting the 3:3'-dinitro-4:4'-diaminodiphenylmethane with a hydrogen-generating mixture, for instance with hydrochloric acid and iron or tin.

The 3:3'-dinitro-4:4'-diaminodiphenylmethane is, in turn, produced by nitration of 4:4'-diaminodiphenylmethane. The nitration is carried out by reaction with nitric acid by a conventional method. Preferably the amino groups of the 4:4'-diaminodiphenylmethane are protected during the nitration by conversion, for example, into acetylamino and other acylamino groups. The conversion of the amino groups can be effected by reacting 4:4'-diaminodiphenylmethane with the corresponding acid anhydride or acyl halide, and after the nitration has been carried out, the amino groups can be regenerated by hydrolysis, for instance with an aqueous solution of an alkali metal hydroxide.

Alternatively, 3:3'-dinitro-4:4'-diaminodiphenylmethane can be produced by rearrangement of N,N'-methylene-bis-o-nitroaniline of the formula

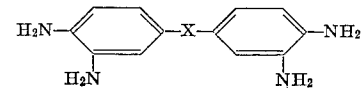


VI

The rearrangement is preferably carried out initially in the presence of excess concentrated hydrochloric acid at a moderate temperature, for example, a temperature within the range of from 20° to 55° C. and subsequently at a higher temperature, for example, a temperature within the range of from 60° to 100° C. in the presence of gaseous hydrogen chloride. The 3:3'-dinitro-4:4'-diaminodiphenylmethane product is isolated and purified by conventional methods. The 3:3'-dinitro-4:4'-diaminodiphenylmethane is then converted to 5:5'-methylene-bis-benzotriazole by the procedure described above.

The N,N'-methylene-bis-o-nitroaniline is, in turn produced for example, by condensing two molecules of o-nitroaniline with one molecule of formaldehyde in an organic solvent, for instance methylated spirits, at an elevated temperature. The product is isolated by conventional methods such as distillation, and can be further purified, for example by recrystallization techniques.

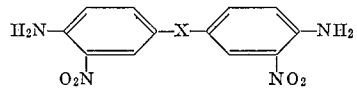
Bis-benzotriazole derivatives of Formula III are produced by reacting a 3:3':4:4'-tetraaminodiphenyl derivative of the formula



VII

wherein X has the same meaning as in Formula III, with nitrous acid or with a compound capable of forming nitrous acid under the conditions of the reaction, in the stoichiometric amounts required to diazotize only two of the four amino groups. The 3:3':4:4'-tetraaminodiphenyl derivative can be treated, for example, with a mixture of an alkali metal nitrite and an inorganic or organic acid. If desired, the reaction can be carried out under conditions similar to a conventional diazotization method, for example, by treatment at a controlled temperature with an aqueous mixture of an alkali metal nitrite and hydrochloric acid, acetic acid or other inorganic or organic acid. The desired bis-benzotriazole derivative of Formula III is then formed by simultaneous elimination of two molecules of water under the diazotization conditions.

The 3:3':4:4'-tetraaminodiphenyl derivative of Formula IV is produced, for instance, by reduction of the corresponding 3:3'-dinitro-4:4'-diaminodiphenyl derivative of the formula



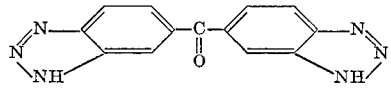
VIII

wherein X has the same meaning as in Formula III.

The reduction is carried out by treating the 3:3'-dinitro-4:4'-diaminodiphenyl derivative with molecular hydrogen in the presence of a catalyst; the hydrogenation catalyst can be, for example, Raney nickel. The reduction can also be carried out in practice by contacting the 3:3'-dinitro-4:4'-diaminodiphenyl derivative with a hydrogen-generating mixture, for instance with hydrochloric acid and iron or tin.

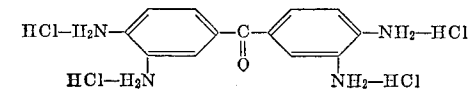
The 3:3'-dinitro - 4:4'-diaminodiphenyl derivative is in turn, produced by nitration of the corresponding 4:4'-diaminodiphenyl derivative with nitric acid by a conventional method. Preferably, the amino groups of the 4:4'-diaminodiphenyl derivatives are protected during the nitration by conversion, for example, to acetylamino or other acylamino groups. The conversion of the amino groups is effected by reacting the 4:4'-diaminodiphenyl derivative with the corresponding acid anhydride or acyl halide, and, after the nitration has been effected, regenerating the amino groups by hydrolysis, for instance with an aqueous solution of an alkali metal hydroxide.

Particular examples of bis-benzotriazole derivatives falling under Formula III can also be obtained by slightly modified methods. For instance, bis-(benzotriazolyl-5) ketone of the formula



IX

can be produced by nitrating 4:4'-dichlorobenzophenone using, for instance, fuming nitric acid at a low temperature, for example a temperature within the range of from −10° to +10° C. and reacting the resulting 4:4'-dichloro-3:3'-dinitrobenzophenone with ammonia, preferably in a closed vessel and at an elevated temperature, for example a temperature within the range of from 100° to 300° C. and preferably in the presence of an organic solvent, for instance ethanol, to produce 4:4'-diamino-3:3'-dinitrobenzophenone, if desired, purifying the product by recrystallization, for example, from pyridine; hydrogenating the 4:4' - diamino - 3:3' - dinitro-benzophenone in the presence of a conventional hydrogenation catalyst, for example, Raney nickel, and preferably in an organic solvent, e.g. dioxan, removing the catalyst, and thereafter saturating the reaction mixture with gaseous hydrogen chloride to produce the tetrahydrochloride of 3:3'-4:4'-tetraaminobenzophenone having the formula



X

and reacting the tetrahydrochloride with a diazotizing agent, e.g., sodium nitrite in an aqueous medium, in such stoichiometric proportions as to diazotize only two of the four amino groups, to form the desired bis(benzotriazolyl-5)ketone of the Formula VIII.

Bis-(benzotriazolyl-5)ketone can also be produced by the controlled oxidation of the bis - (benzotriazolyl) methane of Formula II. Similarly, bis-(benzotriazolyl-5) sulfone can be produced by the controlled oxidation of bis-(benzotriazolyl-5)sulfide.

The following examples further illustrate the present invention. Parts by weight shown therein bear the same relation to parts by volume as do kilograms to litres. Percentages and parts are expressed by weight unless otherwise stated.

EXAMPLE 1

5:5'-methylene-bis-benzotriazole

(A) 4:4' - diacetamino-3:3'-dinitrodiphenylmethane.—562 parts of acetic anhydride were added to a solution of 496 parts of 4:4'-diaminodiphenylmethane in 496 parts by volume of benzene at 30° to 35° C. over a period of 3 hours. The mixture was then stirred at the same temperature for a further period of 1½ hours before being poured into an excess of cold water. The solid product formed was filtered off, recrystallised from glacial acetic acid and dried in a vacuum oven. 596 parts of 4:4'-diacetaminodiphenylmethane, having melting point 236° C. were obtained, representing a yield of 84.5% theoretical.

(B) 4:4' - diacetamino - 3:3' - dinitrodiphenylmethane.—282.4 parts of 4:4'-diacetaminodiphenylmethane were added a little at a time, with stirring, over a period of 30 minutes, to a mixture of 900.3 parts of 70% nitric acid and 1531.5 parts of acetic anhydride at a temperature of 50° C. The nitration mixture was then stirred at 50° C. for a further period of 1½ hours and then allowed to cool and stand at room temperature overnight. The precipitated reaction product was filtered off, washed with water and oven-dried. In this way 144 parts of 4:4'-diacetamino-3:3'-dinitrodiphenylmethane were produced, having melting point 264° C. representing a yield of 38.6% theoretical.

(C) 4:4' - diamino - 3:3' - dinitrodiphenylmethane.—A mixture of 144 parts of 4:4'-diacetamino 3:3'-dinitrodiphenylmethane, 62 parts of sodium hydroxide, 93 parts by volume of water and 1000 parts by volume of 2-methoxyethanol were heated under reflux conditions for 15 minutes and then allowed to cool to room temperature. The orange-red crystalline product which separated was filtered off, washed well with water and oven-dried. In this way 97.7 parts of 4:4'-diamino 3:3'-dinitrodiphenylmethane were obtained, having melting point 238° C., representing a yield of 87.7% theoretical.

(D) 3:3':4:4'-tetraaminodiphenylmethane.—97.7 parts of 4:4'-diamino-3:3'-dinitrodiphenylmethane dissolved in 500 parts by volume of dioxan were hydrogenated in the presence of Raney nickel in a rocking autoclave at a temperature of 100° C. under an initial pressure of hydrogen of 50 atmospheres. The reaction mixture was cooled and filtered to remove the catalyst. The dioxan solvent was removed by distillation under reduced pressure leaving a solid residue which was then washed with methanol. In this way 51 parts of 3:3':4:4'-tetraaminodiphenylmethane were produced having melting point 135° C., representing a yield of 65.9% theoretical.

(E) 5:5'-methylene-bis-benzotriazole.—27.6 parts of sodium nitrite dissolved in 48 parts of water were added, with stirring, to a solution of 45.6 parts of 3:3':4:4'-tetraaminodiphenylmethane in 48 parts of glacial acetic acid and 120 parts of water. The temperature of the reaction mixture rose rapidly to 95° C. and on cooling the reaction mixture, a brown solid separated which was filtered off, washed with water and oven dried. In this way 40 parts of 5:5'-methylene-bis-benzotriazole were obtained, having

melting point 153° C. (d.), representing a yield of 79.1% theoretical.

EXAMPLE 2

A specimen from the same bright acid dipped copper foil was immersed in one of each of the following solutions: 0.01% w./v. aqueous solution of benzotriazole; 0.01% w./v. aqueous solution of 5:5'-methylene-bis-benzotriazole (as produced in the procedure described in Example 1); 0.01% w./v. solution of benzotriazole in industrial methylated spirits; 0.01% w./v. solution of 5:5'-methylene-bis-benzotriazole in industrial methylated spirits; 0.1% w./v. solution of benzotriazole in industrial methylated spirits; 0.1% w./v. solution of 5:5'-methylene-bis-benzotriazole in industrial methylated spirits. The six immersed specimens were maintained at 65° C. for five minutes and they were then washed in distilled water and dried in hot air.

The resistance to tarnishing of the copper specimens was compared with that of a seventh specimen of the same acid-dipped, but otherwise untreated, copper foil as a control, by exposing the specimens to an atmosphere containing 10 parts per million by weight of hydrogen sulphide. The time taken for the onset of visible tarnish to occur was recorded as a measure of tarnish resistance.

The results are shown in the following Table 1:

Table 1

Copper specimen:	Time (in minutes)
Control	2
Treated with 0.01% w./v. aqueous benzotriazole	10
Treated with 0.01% w./v. aqueous 5:5'-methylene-bis-benzotriazole	20
Treated with 0.01% w./v. industrial methylated spirits solution of benzotriazole	10
Treated with 0.01% w./v. industrial methylated spirits solution of 5:5'-methylene-bis-benzotriazole	20
Treated with 0.1% w./v. industrial methylated spirits solution of benzotriazole	10
Treated with 0.1% w./v. industrial methylated spirits solution of 5:5'-methylene-bis-benzotriazole	>30

These results demonstrate that the compound having the Formula II protects copper against tarnishing and that the protective properties are superior to those offered by benzotriazole.

EXAMPLE 3

A specimen from the same sheet of cadmium foil was immersed in one of the following solutions: 0.01% solution of 5:5'-methylene-bis-benzotriazole in industrial methylated spirits; 0.01% solution of 5:5'-methylene-bis-benzotriazole in water. The two immersed specimens were maintained at 65° C. for five minutes and they were then washed in distilled water and dried in hot air.

The resistance to tarnishing of the cadmium specimens was compared with that of an untreated specimen of the same cadmium foil as a control by exposing the four specimens to an atmosphere containing 10 parts per million by weight of hydrogen sulphide. The time taken for the onset of visible tarnish to occur was recorded as a measure of tarnish resistance.

The results are given in the following Table 2:

Table 2

Cadmium specimen:	Time (in hours)
Control	2 to 4
Treated with 0.01% aqueous 5:5'-methylene-bis-benzotriazole	>24
Treated with 0.01% industrial methylated spirits solution of 5:5'-methylene-bis-benzotriazole	>24

These results demonstrate the effectiveness of the compound of the invention having the Formula II as a tarnish inhibitor for cadmium.

EXAMPLE 4

Samples of bright acid dipped copper were polished with an aqueous isopropanol suspension of an abrasive material containing 84 parts of aqueous 40% isopropanol and 15 parts of α-alumina (abrasive) both with and without the addition of 0.3% weight/weight of 5:5'-methylene-bis-benzotriazole. A sample of the same copper was also polished with a similar abrasive material containing 1% of benzotriazole. The polished specimens of copper were then tested for tarnish inhibition by exposure to an atmosphere containing 10 parts per million by weight of hydrogen sulphide. The time taken for the onset of visible tarnishing to occur was recorded as a measure of the tarnish resistance imparted to the copper surface by the polish used.

The results are shown in the following Table 3:

Table 3

Copper specimen:	Time (in minutes)
Polished with a polishing medium not containing a tarnish inhibitor	5
Polished with a polishing medium containing 0.3% w./w. 5:5'-methylene-bis-benzotriazole	13
Polished with a polishing medium containing 1% benzotriazole	17

These results clearly demonstrate the tarnish inhibiting properties imparted to a copper surface by polishing with a polishing medium containing the compound of the invention having the Formula II.

EXAMPLE 5

Bis-(benzotriazolyl-5) ketone

(A) 4,4'-dichloro-3,3'-dinitrobenzophenone.—65 parts of 4,4'-dichlorobenzophenone were added over 3 hours to 390 parts by volume of fuming nitric acid (d. 1.50) at 0°–2° C. After stirring the reaction mixture at room temperature for one hour thereafter it was poured into excess iced water and the solid product which was precipitated was filtered off. In this way were obtained 82 parts (92.2%) of the dinitro compound M.P. 132° representing a yield of 92.2% theoretical.

(B) 4,4' - diamino-3,3' - dinitrobenzophenone.—31.8 parts of 4,4'-dichloro-3,3'-dinitrobenzophenone were divided into equal quantities and each reacted with 2.1 parts of ammonia in 20 parts by volume of ethanol in sealed glass tubes at 150° to 200° C. for 8 hours. The total yield of diamino compound having M.P. 287° C. isolated after recrystallisation from pyridine was 14 parts representing a yield of 49.7% of the theoretical.

(C) 3,3',4,4'-tetraaminobenzophenone tetrahydrochloride.—14 parts of 4,4'-diamino-3,3'-dinitrobenzophenone were hydrogenated in 500 parts by volume of dioxan in the presence of Raney nickel. The filtered dioxan solution was then saturated with dry hydrogen chloride gas. The tetrahydrochloride of the tetramino compound was filtered off.

(D) Bis - (benzotriazolyl - 5) ketone.—The resulting moist tetrahydrochloride of tetraminobenzophenone was dissolved in 250 parts and treated at 5° with 12.6 parts of sodium nitrite dissolved in 100 parts of water. The yellowish-brown solid that separated was filtered off and reprecipitated from the alkaline solution by addition of hydrochloric acid to neutrality. Further purification was effected by treating the concentrated hydrochloric acid solution of the product with carbon, filtering and then neutralising with caustic soda solution. In this way were obtained 4.5 parts (36.8%) of the bis-benzotriazole, having M.P. 285–6° (d.).

EXAMPLE 6

Bis-(benzotriazolyl-5) ether

(A) 4,4'-diacetaminodiphenyl ether.—450 parts of 4,4'-diaminodiphenyl ether in 900 parts by volume of benzene were treated with 450 parts of acetic anhydride at 30° C. to 45° C. for 1½ hours. After this time the product was filtered, washed with ethanol and then dried to furnish 450 parts (70.5%) of 4,4'-diacetamino diphenyl ether, having melting point 229° C.

Analysis.—Calc'd for ($C_{16}H_{16}N_2O_3$) (percent): C, 67.59; H, 5.76; N, 9.85. Found (percent): C, 67.45; H, 5.50; N, 9.96.

(B) 4,4'-diacetamino-3,3'-dinitrodiphenyl ether.—284 parts of 4,4'-diacetaminodiphenyl ether were added over a period of 15 minutes to a mixture of 1530 parts of acetic anhydride and 900 parts of 70% nitric acid and the reaction mixture kept at 30° C. for 1 hour thereafter. The yellow solid which separated during the time was filtered, washed with glacial acetic acid and then water. In this way were obtained 290 parts (77.5%) of the dinitro compound, having melting point 215° C.

Analysis.—Calc'd for ($C_{16}H_{14}N_4O_7$) (percent): C, 51.34; H, 3.77; N, 14.97. Found (percent): C, 51.19; H, 3.79; N, 14.91.

(C) 4,4' - diamino-3,3' - dinitrodiphenyl ether.—156 parts of 4,4'-diacetamino-3,3'-dinitrophenyl ether dissolved in 2-methoxyethanol (1370 parts) were treated under reflux conditions with 80 parts of sodium hydroxide dissolved in 119 parts of water for a period of 15 minutes. The solid formed was filtered off, washed thoroughly with water and dried. In this manner were obtained 107 parts (89.5%) of the diaminodiphenyl ether, having melting point 174° to 176° C.

Analysis.—Calc'd for ($C_{12}H_{10}N_4O_5$) (percent): C, 49.66; H, 3.47; N, 19.30. Found (percent): C, 49.89; H, 3.67: N, 19.44.

(D) 3,3'-4,4'-tetraaminodiphenyl ether.—100 parts of 4,4' - diamino-3,3'-dinitrodiphenyl ether dissolved in 500 parts by volume of dioxan were hydrogenated in the presence of a Raney nickel catalyst. After filtering the hydrogenated solution, the dioxan was removed by evaporation to provide 75 parts of the crude tetraamino compound, having melting point 140° C. (94.5% yield). This product was used in the stage B without further purification.

Analysis.—Calc'd for ($C_{12}H_{14}O$) (percent): C, 62.59; H, 6.13; N, 24.33. Found (percent): C, 62.68; H, 6.12; N, 23.49.

To 46 parts of the crude 3,3',4,4'-tetraaminodiphenyl ether suspended in 48 parts of glacial acetic acid and 120 parts of water were added 27.6 parts of sodium nitrite dissolved in 48 parts of water and the temperature allowed to rise freely with stirring. The oily product initially formed was replaced by a brown solid which was filtered, washed with water and purified by precipitation from its alkaline solution by the addition of hydrochloric acid until neutrality. In this way were obtained 49 parts (99.1%) of crude benzotriazole. Two recrystallisations from 2-methoxyethanol after carbon treatments provided the desired bisbenzotriazole as a light brown solid, having melting point 243° to 244° C.

Analysis.—Calc'd for ($C_{12}H_8N_6O$) (percent): C, 57.15; H, 3.18; N, 33.34. Found (percent): C, 56.94; H, 3.38; N, 33.08.

EXAMPLE 7

Bis-(benzotriazolyl-5) sulphone

(A) 4,4'-dichloro-3,3'-dinitrodiphenylsulphone.—60.3 parts of 4,4'-dichlorodiphenyl-sulphone were dissolved in 301 parts of concentrated sulphuric acid and then 301 parts of fuming nitric acid (d. 1.50) added slowly keeping temperature at 20° to 40° C. initially, then at 80° C. to give a clear yellow solution from which 83 parts (substantially of theoretical yield 100%) of the dinitro compound, having melting point 202° C. separated on pouring on to water.

(B) 4,4'-diamino-3,3'-dinitrodiphenyl sulphone.—37.7 parts of 4,4'-dichloro-3,3'-dinitrodiphenyl sulphone was treated with 6.8 parts of ammonia dissolved in ethanol at 150° C. for 9 hours. The yellow crystalline product was filtered and washed thoroughly with water until the washings were chloride free. The product, having melting point 309° C. was obtained in almost quantitative yield.

(C) 3,3',4,4'-tetraaminodiphenylsulphone tetrahydrochloride.—30 parts of 4,4'-diamine-3,3'-dinitrodiphenyl sulphone dissolved in 500 parts by volume of dioxan were hydrogenated in the presence of a Raney nickel catalyst. The dioxan solution was then saturated with hydrogen chloride gas and the precipitated hydrochloride (38.8 parts) separated by filtration and washed with dioxan.

(D) Bis-(benzotriazolyl-5) sulphone.—38.8 parts of the tetrahydrochloride still moist with dioxan was dissolved in 200 parts of water, this aqueous solution filtered and treated at 5° C. for 10 minutes, and then at 80° C. for 5 minutes with 25 parts of sodium nitrite dissolved in 100 parts of water. The buff-coloured precipitate was filtered off, washed with water and dried. Purification was effected firstly by neutralising an alkaline solution of the product after filtration and secondly by neutralising, with ammonia, a hydrochloric acid solution of the product obtained after filtering. In this way were obtained 9 parts (33.3%) of the bisbenzotriazole having melting point 300° C. (d.) as a cream coloured solid.

EXAMPLE 8

Bis-(benzotriazolyl-5)

4 parts of 3,3'-diaminobenzidine tetrahydrochloride (obtained from BDH) dissolved in 50 parts of water was treated with 2.8 parts of sodium nitrite dissolved in 25 parts of water at 5° C. and then at 80° C. for 30 minutes. The light brown precipitate that separated was filtered off and dried to provide 2.3 parts (96%) of the bisbenzotriazole, having melting point 320° C. and the following elemental analysis by weight:

Analysis.—Calc'd (percent): C, 56.67; H, 3.97; N, 33.06. Found (percent): C, 56.86; H, 3.74; N, 32.46.

EXAMPLE 9

Bis-(benzotriazolyl-5) methane or 5:5'-methylene bis-benzotriazole

To 200 parts o-nitroaniline dissolved in 2000 parts by volume of industrial methylated spirits was added 100 parts 40% formaldehyde solution and after heating on a steam bath for a short time, 2000 parts by volume of liquid were removed by distillation under reduced pressure.

To 186 parts of the residue, having melting point 195° C., were added 1860 parts of concentrated hydrochloric acid and the mixture maintained at 30° C. to 40° C. and then at 80° to 90° C. with the passage of hydrogen chloride gas. The initial yellow crystalline product slowly dissolved to give an orange solution from which yellow crystals later separated. (Reaction time 3½ hours.) These crystals were filtered off, washed with concentrated hydrochloric acid and then digested with hot water to provide 126 parts of the required product (67.7% yield) as an orange-red solid having melting point 230° to 234° C.

The remaining procedure for converting the 4:4'-diamino-3:3'-dinitrophenyl methane to 5:5'-methylene bis-benzotriazole is the same as that described in Example 1, Parts D and E.

We have observed that although 5:5'-methylene-bis-benzotriazole melts at 153° C. it resolidifies and results at 240° C. Possibly, therefore this substance exists in two forms one of which is more thermodynamically stable.

The elemental analysis by weight for the higher-melting form is as follows:

Analysis.—(On product with melting point 240° C.) Calc'd for ($C_{13}H_{10}N_6$) (percent): C, 62.37; H, 4.04; N, 33.59. Found (percent): C, 62.29; H, 4.07; N, 33.18.

EXAMPLE 10

Bis-(benzotriazoly-5-)-1:2-ethane

(A) 4,4'-dinitrodibenzyl.—274 parts of p-nitrotoluene and 464 parts of isoamyl formate dissolved in 250 parts by volume of toluene were added to a suspension of 272 parts of sodium ethoxide in 500 parts by volume of toluene at 0° to 2° C. over 2 hours. The mixture was then stirred for a further 21 hours at 0° to 5° C. and poured into water. In this way, 136 parts (50% yield) of the dinitro compound, having melting point 176° to 176.5° C. were obtained.

(B) 4,4'-diaminodibenzyl.—150 parts of 4,4'-dinitrodibenzyl dissolved in 500 parts by volume of dioxan were hydrogenated in the presence of a Raney nickel catalyst. The filtered dioxane solution was evaporated to dryness. The crude diamino compound, M.P. 136° C. was obtained in substantially quantitative yield.

(C) 4,4-diacetaminodibenzyl.—The 116 parts of crude diamino compound was suspended in 400 parts by volume of benzene and treated with 118 parts of acetic anhydride at 40° to 50° C. for 3 hours. The solid product was separated by filtration and washed with a little acetic acid, then water and finally with benzene. In this way 127.5 parts of 4:4'-diacetaminodibenzyl were obtained having melting point 272° C.

(D) 4:4'-diacetamino - 3:3' - dinitrodibenzyl.—A solution of 482 parts by volume of 70% nitric acid and 731.86 parts by volume of acetic anhydride was made up at 5° C., and 127.5 parts of 4:4'-diacetaminodibenzyl added to this solution at 25° C. over a period of 15 minutes. The resulting mixture was then heated at 50° to 70° C. for a period of one and a half hours. On cooling the reaction mixture in ice, a small amount of solid material was precipitated and the remaining solid product was obtained by adding water to the reaction mixture and cooling in ice. In this way 29 parts of 4:4'-diacetamino-3:3'-dinitrodibenzyl were obtained having melting point 270° to 272° C. and having the following elemental analysis by weight

Analysis.—Calcd., for ($C_{14}H_{14}N_4O_4$) (percent): C, 55.96; H, 4.7; N, 14.5. Found (percent): C, 56.0; H, 5.0; N, 13.98.

(E) 4:4'-diamino-3:3'-dinitrodibenzyl.—A mixture of 23 parts of 4:4'-diacetamino-3:3'-dinitrodibenzyl, 9.6 parts of caustic soda, 19 parts by volume of water and 200 parts by volume of 2-methoxyethanol was heated under reflux conditions for 15 minutes. The reaction mixture was then cooled in ice and the red solid which precipitated from the cooled reaction mixture was separated by filtration and washed with water and then with cold 2-methoxyethanol. In this way, 15 parts of 4:4'-diamino-3:3'-dinitrodibenzyl were produced (representing a yield of 82.7% of the theoretical) having a melting point of 286° to 287° C.

(F) 3:3':4:4'-tetraaminodibenzyl.—15 parts of 4:4'-diamino-3:3'-dinitrodibenzyl dissolved in 250 parts by volume of dioxane were hydrogenated in the presence of a Raney nickel catalyst. After filtering the hydrogenated solution, the dioxane solvent was removed by evaporation to provide the crude tetraamino compound.

(G) Bis-(benzotriazolyl - 5) - 1:2 - ethane.—The crude tetra-amino compound was dissolved in water, this aqueous solution filtered and treated at 5° C. for 10 minutes, and then at 80° C. for 5 minutes with sodium nitrate dissolved in water. The precipitate so formed was filtered off, washed with water and dried. Purification of the product was effected firstly by neutralising an alkaline solution of the product after filtration, and secondly by nuetralising with ammonia, a hydrochloric acid solution of the product obtained after filtering. In this way bis-(benzotriazolyl-5-)-1:2-ethane was obtained.

EXAMPLE 11

Bis-(benzotriazolyl-5)-1:1-cyclohexane

(A) 4,4'-diaminodiphenyl - 1,1 - cyclohexane.—To 475 parts of aniline dissolved in 440 parts by volume of concentrated hydrochloric acid was added 250 parts cyclohexanone and 52 parts by volume of alcohol and the mixture was heated on a steam bath for 12 days. By filtering off the solid that separated on cooling, dissolving this in water and treating with excess alkali, 132.3 parts of the diamino compound having melting point 114° C. were obtained.

(B) 4,4' - diacetaminodiphenyl-1,1-cyclohexane.—42.5 parts of the diaminodiphenylcyclohexane dissolved in 300 parts by volume of benzene were added 36 parts of acetic anhydride and the mixture kept at 40° to 50° C. for 3 hours. The product was separated by filtration and gave 55.2 parts (98.9%) of the diacetyl compounds having melting point 266° to 227° C.

(C) 4:4' - diacetamino-3:3'-dinitrodiphenyl-1:1-cyclohexane.—This 4:4' - diacetamino-diphenyl - 1:1 - cyclohexane was added to a mixture of 70% nitric acid and acetic anhydride at 0° to 5° C. and the mixture stirred at 40° to 50° C. for a period of 1½ hours after the completion of the addition. Water, in small amounts, was added to the nitration mixture to facilitate the separation of the solid product. In this way the 4:4'-diacetamino-3:3'-dinitrodiphenyl-1:1-cyclohexane was obtained.

(D) 4:4' - diamino - 3:3' - dinitrodiphenyl-1:1-cyclohexane.—To the 4:4' - diacetamino-3:3'-dinitrodiphenyl-1:1-cyclohexane suspended in 2-methexyethanol was added sodium hydroxide dissolved in water, and the resulting mixture heated under reflux conditions for 15 minutes. The addition of excess water to the reaction mixture after cooling caused the separation of the 4:4'-diamino-3:3'-dinitrodiphenyl-1:1-cyclohexane.

(E) 3:3':4:4' - tetraaminodiphenyl-1:1-cyclohexane.—The 4:4'-diamino - 3:3' - dinitrodiphenyl-1:1-cyclohexane dissolved in dioxane was hydrogenated in the presence of a Raney nickel catalyst. After filtering the hydrogenated solution, the dioxane solvent was removed by evaporation to provide the crude tetraamino product.

(F) Bis-(benzotriazolyl - 5) - 1:1 - cyclohexane.—The crude tetraamino compound was dissolved in water, this aqueous solution filtered and treated at 5° C. for 10 minutes, and then at 80° C. for 5 minutes with sodium nitrite dissolved in water. The precipitate so formed was filtered off, washed with water, dried and purified in the manner described in Example 10, Part G. In this way bis-(benzotriazolyl-5)-1:1-cyclohexane was obtained.

EXAMPLE 12

Bis(benzotriazolyl-5)-2:2-propane

(A) 4,4'-diaminodiphenyl-2.2-propane.—To 465.6 parts of aniline dissolved in 440 parts of concentrated hydrochloric acid added 145 parts of acetone and 52 parts by volume of ethanol and the reactants heated under reflux conditions for 12 days. Distillation of the residue after neutralisation gave a fraction with alkali having boiling point 192–213° C. per millimetre of mercury pressure in which on recrystallisation from methanol gave 33 parts of the diamino compound having melting point 132° C.

(B) 4.4'-diacetaminodiphenyl-2,2-propane. — To 33 parts of the diamino compound dissolved in 60 parts by volume benzene were added 29.9 parts of acetic anhydride and the mixture kept at 40° to 50° C. for 3 hours; at the end of this time the solid product was separated by filtration and dried. In this way were obtained 38 parts (84%) of the diacetyl compound, melting point 250° to 252° C.

(C) 4.4'-diacetamino - 3,3' - dinitrodiphenyl-2,2 - propane.—38 parts of the 4,4'-diacetaminodiphenyl propane were added to a mixture of 55 parts of 70% nitric acid

and 198 parts of acetic anhydride at 0°–5° C. and the mixture kept at 40° to 50° C. for 1½ hours after the completion of the addition. Water, in small amounts, was added to the orange coloured nitration mixture to facilitate the separation of the product. In this way were obtained 26 parts (55.6%) of the dinitro compound having a melting point 190° C.

(D) 4.4' - diamino-3.3'-dinitrodiphenyl-2,2-propane.—To 26 parts of 4,4-diacetamino-3,3'-dinitrodiphenyl propane suspended in 400 parts by volume of 20 methoxyethanol were added 8.4 parts of sodium hydroxide dissolved in 11.5 parts of water and the mixture refluxed for 15 minutes. The addition of excess water to the reaction mixture after cooling caused the separation of the diaminodinitrodiphenylpropane as an orange solid, having melting point 214° C. The yield was 14 parts (66%).

(E) 3.3' - 4,4' - tetraaminodiphenyl-2,2 - propane (in progress).—14 parts of the diaminodinitrodiphenylpropane were hydrogenated in a 250 parts by volume of dioxan solvent in the presence of a Raney nickel catalyst. After filtering the hydrogenated solution, the dioxane solvent was removed by evaporation to provide 11.35 parts of the crude tetraamino compound.

(F) Bis-(benzotriazolyl-5)-2:2-propane.—The crude tetraamino compound was dissolved in water, this aqueous solution filtered and treated at 50° C. for 10 minutes, and then at 80° C. for 5 minutes with sodium nitrate dissolved in water. The precipitate so formed was filtered off, washed with water, dried and purified in the manner decribed in Example 10, Part G. In this way bis-(benzotriazolyl-5)-2:2-propane was obtained.

EXAMPLE 13

A specimen from the same bright acid-dipped copper foil was immersed in one of each of the following solutions:

0.01%, 0.1%, 0.5% weight/volume aqueous solution of benzotriazole;

0.01% weight/volume solution of bis-(benzotriazolyl-5) ketone in a mixture of 90 parts of water and 10 parts of methylated spirits;

0.01% weight/volume solution of bis-benzotriazole in a mixture of 90 parts of water and 10 parts of methylated spirits;

0.01% weight/volume aqueous solution of 5.5'-methylene-bis-benzotriazole;

0.01% weight/volume aqueous solution of bis-(benzotriazolyl-5) ether.

The seven immersed specimens were maintained at 65° to 70° C. for two minutes and were then removed and dried with warm air.

The resistance to tarnishing of the copper specimens was compared with that of an eighth specimen of the same acid-dipped but otherwise untreated copper foil as a control by heating each sample at 145° C., the appearance of each sample being continuously noted. The times indicated in the following Table 4 are the times at which the first sign of tarnish occurred.

Table 4

Solution in which copper specimen was immersed:	Time, minutes
Control	5
0.01% w./v. aqueous benzotriazole	5
0.1% w./v. aqueous benzotriazole	5
0.5% w./v. aqueous benzotriazole	5
0.01% w./v. aqueous alcohol bis(benzotriazolyl - 5)ketone	10 to 15
0.01% w./v. aqueous alcohol bis-benzotriazole	10 to 15
0.01% w./v. aqueous 5:5'-methylene-bis-benzotriazole	15 to 20
0.01% w.v. aqueous bis-(benzotriazolyl-5)ether	15 to 20

The results summarized in Table 4 clearly demonstrate the improved resistance of copper to tarnishing at an elevated temperature when treated by a process of the present invention, compared with untreated copper and copper treated with benzotriazole. Moreover, it was noted that in contradistinction to the control specimen, the specimens treated according to this invention showed only a moderate degree of tarnishing in that colour of tarnish was a uniform golden brown—the control specimen being very dark brown in colour.

EXAMPLE 14

(A) Samples of bright acid dipped copper were polished with a water emulsifiable polish containing 0.2% weight/weight of bis-benzotriazole, 5:5'-methylene-bis-benzotriazole, bis-(benzotriazolyl-5)ketone and bis-(benzotriazolyl-5)ether. A sample of the same copper was also polished with the same water emulsifiable polish containing no bis-benzotriazole compound. The water emulsifiable soap consisted of 25 parts of red iron oxide (jeweller's rouge), 1 part of hydroxymethyl cellulose, as gelling agent, 13.1 parts of soap consisting of 4.5 parts of triethanolamine and 8.6 parts of stearic acid, 3.2 parts of glycerol and 56.7 parts of water. The polished specimens were then tested for tarnish inhibition by exposing the specimens to an atmosphere containing 10 parts per million by weight of hydrogen sulphide. The time taken for the onset of visible tarnishing to occur was recorded as a measure of the tarnish resistance imparted to the copper surface by the polish used.

The results are summarized in the following Table 5:

Table 5

Active ingredient of polish with which copper specimen was treated:	Time, minutes
Control	2
0.2% bis-benzotriazole	3
0.2% 5:5'-methylene-bis-benzotriazole	3
0.2% bis-(benzotriazolyl-5) ketone	3
0.2% bis-(benzotriazolyl-5) ether	3

These results demonstrate the improved resistance to sulphide tarnishing of copper specimens polished with polishes of the present invention.

(B) Samples of bright acid dipped copper were polished with a polish consisting of an aqueous isopropanol suspension of an abrasive material consisting of α-alumina and also containing a 0.2% weight/weight of 5:5'-methylene-bis-benzotriazole and 0.2% weight/weight of bis-(benzotriazolyl-5) ether. A sample of the same copper was also polished with the same polish but containing no bis-benzotriazole compound. The copper samples were tested for tarnish resistance as described in Example 14A.

The results are summarised in the following Table 6:

Table 6

Active ingredient of polish:	Time, minutes
Control	2
Bis-(benzotriazolyl-5) ether	6
5:5'-methylene-bis-benzotriazole	8

These results clearly demonstrate the improved resistance to sulphide tarnishing of copper specimens treated with polishes of the present invention.

EXAMPLE 15

A specimen from the same bright acid dipped copper foil was immersed in one of each of the following solutions:

(i) 2.5% weight/volume of bis-(benzotriazolyl-5)-methane, in industrial methylated spirits

(ii) 5.0% weight/volume of bis-(benzotriazolyl-5)-methane in industrial methylated spirits

(iii) 2.5% weight/volume of bis-(benzotriazolyl-5)-ether in industrial methylated spirits

(iv) 5.0% weight/volume of bis-(benzotriazolyl-5)-ether in industrial methylated spirits

(v) 2.5% weight/volume of benzotriazole in industrial methylated spirits

(vi) 5.0% weight/volume of benzotriazole in industrial methylated spirits

The six immersed specimens were maintained at 65° C. for two minutes and then washed in distilled water and dried in hot air.

The resistance to tarnishing of the copper specimens was compared with that of a tenth specimen of the same acid-dipped, but otherwise untreated, copper foil as a control, by exposing the specimens to an atmosphere containing 10 parts per million by weight of hydrogen sulfide. The time taken for the onset of visible tarnish to occur was recorded as a measure of tarnish resistance.

The results are shown in the following table:

Copper specimen:	Time, minutes
Control	2
(i) Treated with 2.5% bis-(benzotriazolyl)-methane	15
(ii) Treated with 5.0% bis-(benzotriazolyl)-methane	25
(iii) Treated with 2.5% bis-(benzotriazolyl)-ether	15
(iv) Treated with 5.0% bis-(benzotriazolyl)-ether	25
(v) Treated with 2.5% benzotriazole	10
(vi) Treated with 5.0% benzotriazole	10

These results clearly demonstrate the improved protection afforded by the compositions of the present invention compared with compositions containing benzotriazole.

EXAMPLE 16

Specimens of copper foil were immersed in one of each of the following solutions:

(i) 0.01% weight/volume of benzotriazole in water

(ii) 0.01% weight/volume of bis-(benzotriazolyl)-5)-1:2-ethane in water, the remaining procedure being as described in Example 15. The results are shown in the following table:

Copper specimen:	Time, mins.
Control	2
(i) Treated with 0.01% benzotriazole	10
(ii) Treated with 0.01% bis-(benzotriazolyl-5)-1:2-ethane	30

These results demonstrate the improved protection afforded by the above composition of the invention compared with a composition containing benzotriazole.

EXAMPLE 17

Synthetic ester-based lubricant compositions were produced and subjected to the Pratt and Whitney Type II oxidation-corrosion test with the iron and copper-protecting additives given in column 1 in the amounts (weight percent) given in column 2 of the table below. The base fluid was trimethylol propane tripelargonate and each test was carried out for 48 hours at 425° F. with air at the rate of 5 liters per hour and in the presence of copper and steel.

The results are shown in the following table; the sludge formation is expressed in mg.; and the weight change of the specimens as mg./cm.^{2}.

Additive	Percent by weight of additive	Percent viscosity increase at 100° F.	Sludge, mg.	Weight change of specimen	
				Cu	Steel
Dioctyl diphenylamine	4	52.58	0.3	−2.201	+0.007
Dioctyl diphenylamine plus benzotriazole.	4 0.5	32.64	0.2	−0.155	0
Dioctyl diphenylamine plus bis-(benzotriazolyl-5)-methane.	4.0 .001	31.80	0	−0.218	−0.015

This table shows that similarly satisfactory corrosion-inhibition is obtained on steel and copper with a composition containing dioctyl diphenylamine and, as second corrosion inhibitor, according to the present invention, bis-(benzotriazolyl-5-)methane in only one-fiftieth of the amount in which the second inhibitor must be present if benzotriazole is used as the latter.

EXAMPLE 18

1 kg. of tissue paper is immersed in a 0.01% w./v. aqueous solution of 5:5′ - methylene - bis - benzotriazole, withdrawn from the solution and air-dried.

1 kg. of wrapping paper is treated in the same manner. The resulting materials can be used for wrapping metal articles or articles possessing metallic surfaces which require protection from corrosion and tarnishing.

EXAMPLES 19–22

The mixtures having the compositions set out below were made up:

(A) (Control):
80 parts of pentasodium tripolyphosphate
20 parts of sodium dodecyl benzene sulphonate

(B) (Example 19):
80 parts of pentasodium tripolyphosphate
19.6 parts of sodium dodecyl benzene sulphonate
0.4 part of bis-(benzotriazolyl-5) methane

(C) (Control):
80 parts of pentasodium tripolyphosphate
20 parts of sodium lauryl sulphate

(D) (Example 20):
80 parts of pentasodium tripolyphosphate
19.6 parts of sodium lauryl sulphate
0.4 part of bis-(benzotriazolyl-5) methane

(E) (Control):
80 parts of tetrasodium pyrophosphate
20 parts of sodium dodecyl benzene sulphonate

(F) (Example 21):
80 parts of tetrasodium pyrophosphate
19.6 parts of sodium dodecyl benzene sulphonate
0.4 part of bis-(benzotriazolyl-5) methane

(G) (Control):
80 parts of tetrasodium pyrophosphate
20 parts of sodium lauryl sulphate

(H) (Example 22):
80 parts of tetrasodium pyrophosphate
19.6 parts of sodium lauryl sulphate
0.4 part of bis-(benzotriazolyl-5) methane

0.5% weight/volume aqueous solutions were made up from each of compositions A to H and heated to 70° C. An article of nickel silver cutlery was then immersed in one of the respective solutions and maintained in the hot solution for a period of three days. The appearance of each nickel silver article was noted at regular intervals throughout this period.

The articles immersed in each of the control solutions yellowed within 30 minutes and became almost black within the three day test period. On the other hand, the solutions derived from compositions B, D, F and H (Examples 1, 2, 3 and 4 respectively) showed substantially no staining throughout the test period.

In a further series of tests, a piece of clean copper

was immersed in one of the respective aqueous solutions derived from compositions C, D, E and F. The solutions were maintained at 70° C. and the tests were run for a period of 48 hours.

The control solutions (derived from compositions C and E) were pale blue in colour after the test, whereas the solutions of compositions D and F were clear and colourless.

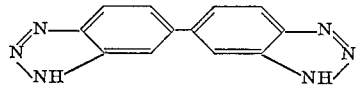
The weight loss suffered by each of the respective copper specimens in the second series of tests is set out in the following table:

Composition:	Weight loss, milligrams/square decimetre
(C) (Control)	37.0
(D) (Example 20)	3.5
(E) (Control)	37.0
(F) (Example 21)	5.5

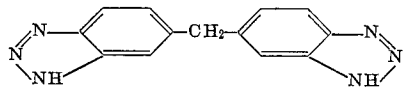
Similar results were obtained when instead of bis-(benzotriazolyl-5) methane, bis-benzotriazole itself or a compound of Formula III was employed.

What is claimed is:

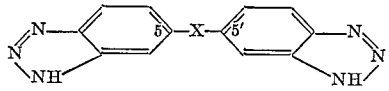
1. A process for treating a metallic surface to inhibit tarnishing and corrosion thereof, comprising contacting the metallic surface with a corrosion-inhibiting amount of a member selected from the group consisting of the bis-benzotriazole of the formula



the 5:5'-methylene-bis-benzotriazole of the formula



and a bis-benzotriazole of the formula



wherein X is selected from the group consisting of (a) divalent straight chain alkylene containing from 1 to 6 carbon atoms in the chain and being substituted with from 1 to 2 alkyl groups containing each from 1 to 4 carbon atoms where the alkylene group contains only 1 carbon atom, or being unsubstituted or substituted with one or more alkyl groups containing from 1 to 4 carbon atoms where the alkylene group contains 2 or more carbon atoms; (b) 1:1-cycloalkyl containing 5 or 6 carbon atoms; (c) a carbonyl group; (d) a sulfonyl group; (e) an oxygen atom; or (f) a sulfur atom.

2. A process as claimed in claim **1** wherein the metal surface is immersed in a solution containing from 0.001% by weight to saturation of said member, calculated on the weight of the solution.

3. A process as claimed in claim **2** wherein the solution contains from 0.01% to 5% by weight of said member, calculated on the weight of the solution.

4. A process as claimed in claim **2** wherein the solution contains from 0.1% to 1.0% by weight of said member, calculated on the weight of the solution.

5. A process as claimed in claim **2** wherein the temperature of the solution is within the range of from 60° to 100° C.

6. A process as claimed in claim **1** wherein the metallic surface is packed in tissue paper or wrapping paper impregnated with said member.

7. A process as claimed in claim **6** wherein the tissue paper or wrapping paper is impregnated by soaking in a solution containing from 0.1% to 5% by weight of said member calculated on the weight of the solution.

8. A process as claimed in claim **1** wherein the metallic surface is exposed to an atmosphere saturated with the vapor of said member.

9. A process as claimed in claim **8** wherein the said vapor is maintained at 85° C.

10. A process as claimed in claim **8** wherein said vapor is maintained at a temperature of from about 100° to 160° C. and the metallic surface is chilled to a lower temperature in order to facilitate rapid condensation of the vapor on said metallic surface.

11. A process as claimed in claim **1** wherein the metallic surface is treated with a non-abrasive wax or polish containing said member.

12. A process as claimed in claim **11** wherein the wax or polish contains from 0.1% to 10% by weight of said member calculated on the weight of said wax or polish.

13. A process as claimed in claim **1** wherein the metallic surface is treated with a suspension of an abrasive material suspended in a medium of from liquid to soft solid consistency which medium contains said member.

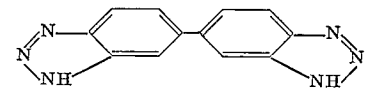
14. A process as claimed in claim **13** wherein the amount of said member present in said medium is within the range of from 0.01% to 5% by weight, calculated on the weight of said medium.

15. A process as claimed in claim **14** wherein the amount of said member present in said medium is within the range of from 0.1% to 1.0% by weight, calculated on the weight of said medium.

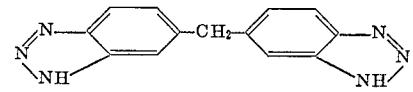
16. A process as claimed in claim **1** wherein the metallic surface is that of copper or a copper alloy.

17. A process as claimed in claim **1** wherein the metallic surface is that of cadmium or a cadmium alloy.

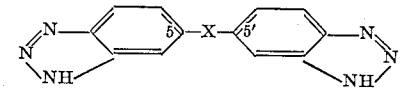
18. A composition for application to a metallic surface, consisting essentially of as tarnishing and corrosion inhibitor, a corrosion-inhibiting amount of a member selected from the group consisting of the bis-benzotriazole of the formula



the 5:5'-methylene-bis-benzotriazole of the formula



and a bis-benzotriazole of the formula



wherein X is selected from the group consisting of (a) divalent straight chain alkylene containing from 1 to 6 carbon atoms in the chain and being substituted with from 1 to 2 alkyl groups containing each from 1 to 4 carbon atoms where the alkylene group contains only one carbon atom, or being unsubstituted or substituted with one or more alkyl groups containing from 1 to 4 carbon atoms where the alkylene group contains 2 or more carbon atoms; (b) 1:1-cycloalkyl containing five or six carbon atoms; (c) a carbonyl group; (d) a sulfonyl group; (e) an oxygen atom; or (f) a sulfur atom.

19. A composition as claimed in claim **18** wherein a further corrosion-inhibitor effective for the protection of ferrous metals is also present in the composition.

20. A composition as claimed in claim **18** consisting essentially of, in addition to said member, an inorganic water soluble phosphate which acts as a sequesting agent for calcium ions, the resulting composition being a detergent composition.

21. A detergent composition as claimed in claim **20** wherein the proportion of said member is within the range of from 0.01% to 5% by weight calculated on the weight of the total composition.

22. A detergent composition as claimed in claim **21**

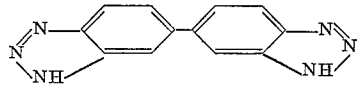
wherein the proportion of said member is within the range of from 0.1% to 1.0% by weight calculated on the weight of the total composition.

23. A detergent composition as claimed in claim 20 which composition additionally contains a cationic, nonionic or anionic surface-active agent.

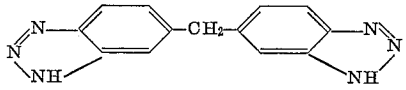
24. A detergent composition as claimed in claim 23 wherein the surface-active agent is an anionic surface-active agent.

25. A detergent composition as claimed in claim 20 which composition additionally contains water in sufficient amount to form an aqueous solution of the composition.

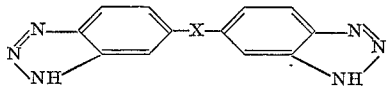
26. A functional composition selected from the group consisting of lubricants, cutting oils, transformer oils, antifreeze compositions and coolant compositions, said functional composition being resistant to deterioration of function through contact with a metal, consisting essentially of, as a metal deactivator, an effective amount of a member selected from the group consisting of the bis-benzotriazole of the formula



the 5:5'-methylene-bis-benzotriazole of the formula



and a bis-benzotriazole of the formula

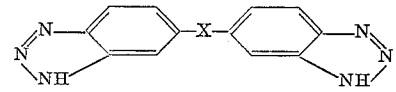


wherein X is selected from the group consisting of (a) divalent straight chain alkylene containing from 1 to 6 carbon atoms in the chain and being substituted with from 1 to 2 alkyl groups containing each from 1 to 4 carbon atoms where the alkylene group contains only 1 carbon atoms, or being unsubstituted or substituted with one or more alkyl groups containing from 1 to 4 carbon atoms where the alkylene group contains 2 or more carbon atoms; (b) 1:1-cycloalkyl containing 5 or 6 carbon atoms; (c) a carbonyl group; (d) a sulfonyl group; (e) an oxygen atom; or (f) a sulfur atom.

27. A functional composition as claimed in claim 26, wherein the functional composition is in contact with copper or a copper alloy.

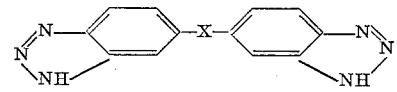
28. A functional composition as claimed in claim 26, further comprising a corrosion inhibitor effective for the protection of ferrous metals.

29. Tarnish and corrosion-inhibiting wrapping paper consisting essentially of, as a corrosion inhibitor, an effective amount of bis-benzotriazole, 5:5'-methylene-bis-benzotriazole of a bis-benzotriazole of the formula



wherein X is selected from the group consisting of (a) divalent straight chain alkylene containing from 1 to 6 carbon atoms in the chain and being substituted with from 1 to 2 alkyl groups containing each from 1 to 4 carbon atoms where the alkylene group contains only 1 carbon atom, or being unsubstituted or substituted with one or more alkyl groups containing from 1 to 4 carbon atoms where the alkylene group contains 2 or more carbon atoms; (b) 1:1-cycloalkyl containing 5 or 6 carbon atoms; (c) a carbonyl group; (d) a sulfonyl group; (e) an oxygen atom; or (f) a sulfur atom.

30. Tarnish and corrosion-inhibiting tissue paper consisting essentially of, as a corrosion inhibitor, an effective amount of bis-benzotriazole, 5:5'-methylene bis-benzotriazole or a bis-benzotriazole of the formula



wherein X is selected from the group consisting of (a) divalent straight chain alkylene containing from 1 to 6 carbon atoms in the chain and being substituted with from 1 to 2 alkyl groups containing each from 1 to 4 carbon atoms where the alkylene group contains only one carbon atom, or being unsubstituted or substituted with one or more alkyl groups containing from 1 to 4 carbon atoms where the alkylene group contains 2 or more carbon atoms; (b) 1:1-cycloalkyl containing 5 or 6 carbon atoms; (c) a carbonyl group; (d) a sulfonyl group; (e) an oxygen atom; or (f) a sulfur atom.

References Cited

UNITED STATES PATENTS

3,171,840	3/1965	Ursprung et al.	252—391 X
3,222,285	12/1965	Rai et al.	252—390 X

LEON D. ROSDOL, Primary Examiner

M. HALPERN, Assistant Examiner

U.S. Cl. X.R.

252—47, 51.5, 50, 75, 77, 78, 152, 390, 391, 392; 260—308