A Review on Recent Patents in Corrosion Inhibitors

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Abstract: Selection of an appropriate corrosion inhibitor, inhibitor combination or package is an exceptionally cost effective and materials saving measure in various industries. Current trends and novel approaches in corrosion inhibitors are reviewed here. Recent developments in the inhibition technology are discussed in accordance with the areas of application of inhibitors.

Keywords: Corrosion inhibitors, patents, R&D.

INTRODUCTION

In spite of much advancement in the field of corrosion science and technology, the phenomenon of corrosion (mainly of Fe, Al, Cu, Zn, Mg and their alloys) remains a major concern to industries around the world. Though the serious consequences of corrosion can be controlled to a great extent by selection of highly corrosion resistant materials, the cost factor associated with the same, favors the use of cheap metallic materials along with efficient corrosion prevention methods in many industrial applications. In this aspect, corrosion inhibitors have ample significance as individual inhibitors or as a component in chemical formulations. They have wide commercial applications such as in cooling waters, oil and gas fields, paints pigments, lubricants etc. [1].

A large number of corrosion inhibitors have been developed and used for application to various systems depending on the medium treated, the type of surface that is susceptible to corrosion, the type of corrosion encountered, and the conditions to which the medium is exposed [2]. The efficiency and usefulness of a corrosion inhibitor under one set of circumstances often does not imply the same for another set of circumstances. In many applications like industrial water treatment systems, a combination of more than one corrosion inhibitor along with other additives such as anti-scalents, biocides and polymeric dispersants are supplied. In many areas, corrosion inhibitors work synchronously with superior coatings and cathodic protection. In spite of the long history of corrosion inhibition; a highly efficient and durable inhibitor that can completely protect iron and low carbon steel in aggressive environments such as high Cl^- electrolyte for longer duration is yet to be realized.

The present article reviews recent (2008-2009) patents reported on corrosion inhibitors. The manuscript brings light to the major outputs in the field of inhibitor technology in the last two years and are presented according to the application area of inhibitors.

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CORROSION INHIBITION IN COOLING WATER SYSTEMS

Corrosion in an open cooling water system is closely related to mineral scale formation, solid deposition and microbiological fouling. Hence a comprehensive cooling water additive composition consists of anti-scaling agents, polymeric dispersants and biocides along with corrosion inhibitors to protect Fe, Cu, Al and their alloys [3]. High content of salt and dissolved oxygen increases the severity of corrosion in open systems. Galvanic corrosion is another serious concern. A successful water treatment is highly economic by reducing inspection shutdowns and permitting extensive use of low carbon steel.

The conventional inorganic inhibitors continue to be a best choice in inhibitor packages. Many of the recent patents contain inhibitors such as silicates, phosphates, molybdates and tungstates as a component in the proposed combination. Azole based compounds continue to be in the frontline as Cu corrosion inhibitor. Zhang *et al.* patented an inhibitor package of sodium silicate, sodium tungstate, sodium phosphate/hexametaphosphate and benzotriazole/mercapto-benzothiazole along with an acrylic co-polymer for desalted circulating cooling water system [4]. Xiao *et al.* patented a scale and corrosion inhibitor composition for circulating cooling water system that comprised of 2-phosphonobutane-1,2,4-tricarboxylic acid, hydroxyethylidene diphosphonic acid, $ZnSO_4.7H_2O$, benzotriazole, sodium hexametaphophate and a co-polymer [5]. However the inorganic inhibitors such as phosphate and chromate are steadfastly becoming the object of federal and local regulations due to environmental concerns. Gernon *et al.* proposed a method of controlling corrosion of Fe and Cu based metals using alkylalkanol-amine based compounds. The compound has the general formula R_x-NH_y-$(CH_2CH_2OH)_z$, where R is C3 to C8 alkyl groups; x and z are 1 or 2; y is 0 or 1 [6]. Iyasu *et al.* patented thioglycolic acid or its salts and azole compounds as pitting inhibitors for Cu substrates [7]. An inhibitor combination of sodium gluconate, benzotriazole, tolyltria-zole, molybdate, tungstate and $ZnSO_4$ was patented by Cao [8].

Increased popularity of high alkalinity, no pH control water treatment programs have resulted in more frequent and severe white rust corrosion issues, especially in cooling

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tower applications. Kidambi *et al.* patented a method for inhibiting white rust corrosion on galvanized surfaces by introducing an effective amount of a corrosion-inhibiting composition that includes one or more thiols based white rust corrosion-inhibiting compounds [9]. Corrosive attack of Cu by NH_3 in water is well known in the water treatment industry, and presents a particular challenge to reuse of wastewater sources that contain ammonia in cooling water systems. Duke and Kubis patented a method of inhibition in this direction that was directed toward the use of azole based inhibitors. Dosages of the azole or a mixture of two or more azoles will be proportional to ammonia/ammonium ion concentration in the cooling water and to increasing TDS concentration and higher pH level, preferably from 0.5 to 60 mg/L residual [10].

For closed cooling water systems (e.g. engine coolants), the problems associated with scaling are very less. Heat transfer fluids, which generally comprise water, glycol or glycol- water mixtures, are in communication with one or several metallic parts that are prone to corrosion. Al is especially vulnerable to corrosion and many vehicles have heads, radiators and other aluminum components in the cooling system. Examples of optional conventional corrosion inhibitors include alkali metal borates, alkali metal silicates, alkali metal benzoates, alkali metal nitrates, alkali metal nitrites, alkali metal molybdates, and hydrocarbyl thiazoles. In a recent patent, Kawaguchi disclosed tourmaline based corrosion inhibitors for antifreezing fluids [11]. A corrosion inhibiting composition of monocarboxylic acid (octanoic acid), dicarboxylic acid (sebacic acid), triazole and triethanolamine compound was patented by Belokurova [12]. An antifreeze composition of triethanolamine phosphate, a non ferrous metal inhibitor, disodium salt of ethylenediaminetetraacetic acid and an antifoaming agent with ethylene glycol balance was disclosed by Belikov [13].

Zou patented an inhibitor composition for circulating and cooling system of automobiles that contains $NaNO_2$, $Na_2B_4O_7.10H_2O$, 1,2,3-benzotriazole and $ZnNO_3$ [14]. Fukutani patented an aqueous solution of glycerin, saturated fatty acids/salts, saturated di/tricarboxylic acids/salts, tolyltriazole and benzotraizole for use in radiator coolants and metalworking solutions [15]. Yuan *et al.* patented an additive composition of a monobasic organic acid, phytic acid, borax, hydroxyphenylhydrazine, carbohydrazide, polyacrylamide, siloxane, benzotriazole, and a siloxane stabilizer for circulating cooling water system of internal combustion engines [16].

Brazed heat exchangers are lower in weight and are able to radiate heat better than heat exchangers formed by mechanical expansion. Yang *et al.* patented a heat transfer fluids intended for use in heat transfer systems comprising brazed metals or metal alloys such as brazed Al. The corrosion inhibitor comprises a combination of inhibitors selected from the group consisting of an azole-based inhibitor, a siloxane-based inhibitor, a silicate, a carboxylate, a tall oil fatty acid, a borate, a nitrate, a nitrite, and an amine salt. In general, the corrosion inhibitors are present in an amount of about 0.01 to about 10 wt%, based on the total weight of the heat transfer fluid [17].

CORROSION INHIBITION IN OIL AND GAS FIELD

The inhibition in oil and gas field is more complicated and requires specialty inhibitors depending on the area of application such as in refineries, wells, recovery units, pipelines etc. Aggressive gases such as H_2S, CO_2, and organic acids complicate the problem of inhibition in wells. Corrosion problems in petroleum refining operations associated with naphthenic acid constituents and sulfur compounds in crude oils have been recognized for many years. It is particularly severe in atmospheric and vacuum distillation units at higher temperatures, 175-400 ^oC. Dissolved O_2 is the main species causing corrosion in recovery units. Dry corrosion is of great importance in refinery processes. HCl may form in refineries as a by-product. O_2, CO_2 and H_2S intensify corrosion problems in natural gas pipelines.

Wet corrosion in refineries can be controlled by passivating, neutralizing or adsorption type inhibitors. Slag inhibitors are used along with the corrosion inhibitors to reduce deposits. Both water soluble and oil soluble inhibitors are used in pipelines. Adsorption type inhibitors are widely used for preventing internal corrosion of pipelines carrying refined petroleum products. In general, where the operating temperatures and/or the acid concentrations are higher, a proportionately higher amount of the corrosion inhibitor composition will be required. It is preferable to add the inhibitor composition at a relatively high initial dosage rate, about 2000 to 5000 ppm, and to maintain this level for a relatively short period of time until the presence of the inhibitor induces build-up of a corrosion protective coating on the metal surfaces. Once the protective coating is established, the dosage may be reduced to an operational range, about 10 to 100 ppm. It is known that nitrogen based corrosion inhibitors are relatively ineffective in the high temperature environment. Also, the phosphorus-containing compounds may impair the function of various catalysts used to treat crude oil.

Catalytic polymerization of tall oil fatty acids such as oleic and linoleic acids give varying amounts of dimerized and trimerized fatty acids. These dimer and/or trimer fatty acids may be neutralized with an appropriate amine; which the oil industry has traditionally employed as an oil-soluble inhibitor for reducing corrosion in oil well piping and related recovery equipment. Over the years, the corrosion inhibition art has looked for alternatives to the dimer/trimer acid-based product. Of particular interest in this regard is the class of fatty acid-based products which have been functionalized with maleic anhydride and/or fumaric acid. The fatty acids can first be maleated followed by an oxidation. Alternatively, the fatty acid material can first be oxidized and then the oxidized fatty acid product can be maleated [18]. Zagidullin *et al.* patented a terephthalic acid based method for corrosion inhibition. An acid inhibitor is prepared by interaction of polyethylene-polyamine with terephthalic acid at 150-190 ^oC for 4-8 h in the molar ratio of 2:1, followed by reaction with benzyl chloride at 80 ^oC for 5 h. The product was used as a component along with urotropin and neonol in water [19]. Rhodanine (2-thioxo-4-thiazolidinone) and its 3- or 5- derivatives are patented as a Fe corrosion inhibitor of oil refining equipment in carbonic acid derivatives [20].

Zetlmeisl *et al.* disclosed a method for inhibiting naphthenic acid corrosion at high temperatures based on novel thiophosphorus compounds [21]. Subramaniyan *et al.* patented a polyisobutylene phosphorous sulfur compound as corrosion inhibitors for high temperature naphthenic acid corrosion and sulphur corrosion. This results in improved performance as well as a decreased phosphorus requirement. The compound is obtained by reaction of high reactive polyisobutylene with P_2S_5 in presence of sulphur powder [22]. Huang *et al.* patented a reaction product of thiophosphate (produced by reaction of phosphide with fatty alcohols) with spiro-diester (product of reaction of alkenyl succinic anhydride with organic amine using inorganic salts as catalyst) as high temperature corrosion inhibitor [23]. Alykov *et al.* patented 1-nitro-3,3-diphenyl-1-[3-(3-nitrophenyl)-1,2,4-oxydiazol-5-yl]-2,3-diazoprop-1-ene, that was obtained by condensation reaction of equimolar quantities of substituted 3-aryl-5-nitromethyl-1,2,4-oxadiazol with 1,1-diphenylhydrazine in ethoxyethane medium; as corrosion inhibitor for metal protection against acid corrosion in oil and gas pipelines for non-alloyed steels [24]. Strak *et al.* patented a method for inhibiting corrosion in a separation unit that comprising treating the unit with inhibitors selected from the group consisting of dodecenyl succinic acid, and di-hexyl succinic acid [25]. Leinweber patented low toxic, water soluble and biodegradable corrosion inhibitors of metal salts of $CH_3SCH_2CH_2CH$ (NHCOR)COOH containing anionic and cationic surfactants [26, 27].

Bhat *et al.* disclosed a non chromate aqueous corrosion inhibitor composition for metallic surfaces exposed to medium of pH 4, comprising of an anodic corrosion inhibitor (ammonium heptamolybdate/sodium orthovanadate), a cathodic corrosion inhibitor (cerium chloride) and a metal complexing ligand (trisodium citrate-2-hydrate); dissolving the blended product in water as 2.5 wt.% solution [28]. N-acetyl-2-(2,3-dihydroxycilopentenyl) aniline with concentrations 50-200 mg/L was proposed as an inhibitor of corrosion in mineralized water petroleum solutions including H_2S [29]. 2-propyl-3-ethyl-8-oxychinoline-$ZnCl_2$ complex was disclosed as a steel corrosion inhibitor for petroleum production applications in mineralized media with high O_2 content. The compound is manufactured by condensation of $ZnCl_2$ containing o-aminophenol with an oil aldehyde in benzene followed by reaction with $ZnCl_2$ [30].

Acidic fluids (HCl, HF etc) are often used as a treating fluid in wells penetrating subterranean formations for clean-up operations or stimulation operations for oil and gas wells. Corrosion inhibitor intensifiers have been used to extend the performance range of a selected acid corrosion inhibitor. Most intensifiers such as KI, Sb-based compounds etc have temperature, time, and environmental drawbacks. Wilson *et al.* disclosed 2-chloro-2,2-diphenylacetic acid and 2-bromo-isobutyric acid as corrosion inhibitor intensifiers [31]. Beloglazov *et al.* disclosed an antipyrine derivative as an inhibitor against microbilogical (myxromycete) corrosion of equipment made of carbon steel and alloy steel with cadmium coating [32].

CORROSION INHIBITORS IN PAINTS AND COATINGS

Inhibitor technology in paints is advanced to great extents with the help of nanotechnology. Nanostructured material's engineering extends the possibility of engineering 'smart' coatings that can release corrosion inhibitors on demand when the coating is breached, stressed or an electrical or mechanical control signal is applied to the coating. Inherently conducting polymer films containing inhibiting anions as the dopant anions can release them when the film is coupled to a breach in the coating. Research has developed chromate- free corrosion inhibiting additives in which organic corrosion inhibitors are anchored to nanoparticles with high surface areas that can be released on-demand [33].

High performance criteria of corrosion inhibitors and coatings are essential in applications such as aircraft industry. The inhibitor and conversion coating materials must be able to prevent detectable pitting corrosion of a coated aluminum alloy substrate even after long salt spray, as long as 3000 h. Boocock patented a non-chromate and highly crystalline hydrotalcite inhibitor for pigment applications. Hydrotalcite, containing the decavanadate ion is the source of corrosion inhibition and is produced by high temperature reaction of a mixture of zinc oxides/hydroxides with aluminum hydroxides and vanadium oxide. The subject compositions are highly effective in providing blister-free corrosion prevention in typical coil and aerospace grade epoxy primer and color coat combinations, to prevent corrosion of aluminum or hot-dip galvanized or galvalume coil stocks [34]. Slaghek *et al.* patented chemically modified polysaccharides as corrosion inhibitors and/or preservatives to a composition suitable for coating solid surfaces [35]. A corrosion inhibitor formula based on crystalline permanganate soldalite compositions was patented for pigment applications [36]. Tayler *et al.* explored synergistic inhibition of anodic (from vanadates, molybdates, tungstates, phosphates, borates) and cathodic inhibitors (from Ce, Y, La, Eu, Gd, and Nd) as suitable substitute for chromates [37].

A complete coating system usually consists of three individual layers; the conversion coating, second primer layer, and the polyurethane topcoat. Organic and inorganic films are commonly used in the pre-treatment stage to create a barrier for aggressive environmental species. Such films were successfully deposited on metallic surfaces by formation of metallo-siloxane bonds, plasma polymerization or sol-gel technique in order to provide an additional barrier against the corrosion species and mainly to improve adhesion between the metal and polymer coating system. However, the inhibitors incorporated directly into the sol-gel matrix loose their activity very quickly. Andreeva *et al.* patented corrosion inhibiting coating for active corrosion protection of metal surfaces comprising a sandwich-like inhibitor complex and to methods for preparing the same. The sandwich-like complex of the corrosion inhibiting coating comprises a first inner layer of organic species, a corrosion inhibitor layer and a second outer layer of organic species. The complex is sensitive to at least one stimulus, e.g. a pH change, and capable to release the corrosion inhibitor in response to the stimulus [38]. Gammel *et al.* patented an anticorrosive paint for metal substrates capable of permanent releasing of a corrosion inhibitor. The coating comprises a matrix consisting of a primer or sol-gel materials containing polymer encapsulated corrosion inhibitor such as mercaptobenzothiazole [39]. Golovin *et al.* patened a method of protecting polymer coated metal from corrosion using inhibitor microcapsules. The polymer coating composition contains microcapsules with corrosion inhibitor with a polymer shell. Microcapsules with the corrosion inhibitor are made of an inert sorbent (porous alumina, porus silica etc) with polymer shell into pores of which the inhibitor is impregnated. The method improves corrosion protection of coated metal surface due to continuous release of inhibitor during operation of coating [40]. Zhu *et al.* suggested an alternative to the pre-treatment step in coating. By incorporating a small percentage of monomeric organofunctional silanes or oligomeric organofunctional silanes into a polymeric coating such as a primer or clear coat, one can eliminate the need for pretreatment. In particular, amino vinyl silane blends are useful in the present invention [41].

Organic-inorganic hybrid composites which comprise an inorganic component and an organic conducting component are known in the art. Jaworowski *et al.* patented an anodic-cathodic corrosion inhibitor-conductive polymer composite. In accordance with the present disclosure, there is provided a conductive polymer corrosion protective coating to be applied to structures such as turbine engine components which includes a conductive polymer with corrosion inhibitive pigments or additives comprising an anodic (vanadate, molybdate, tungstate and/or mixture) and a cathodic corrosion inhibitor (cerium, neodymium, praseodymium, and/or mixture). The hybrid composites can be used in anti-electrostatic, electrostatic dispersion and electromagnetic shielding applications [42].

A corrosion inhibitor in combination with a metal ion scavenger, e.g., a metal chelating agent can act as a quantum dot quenching-preventive agent. When quantum dots are applied to metals such as copper, brass, stainless steel, bronze, aluminum, nickel, etc, the fluorescence intensity of the quantum dots can be dramatically reduced or quenched. In addition, the quantum dots may easily rub off of the substrate materials, particularly smooth materials such as stainless steel and brass. This limits the current use of quantum dots on such metallic surfaces. The respective amounts of the corrosion inhibitor and the metal ion scavenger can be optimized to prevent the quenching of the quantum dots in the presence of the metal ions [43].

ACID CORROSION INHIBITORS

Inhibitors for acid corrosion, especially for Fe and steel have widespread use in different industries (e.g. oil and gas field). Mostly organic inhibitors are employed as acid inhibitors; as the passivating inorganic inhibitors may be dangerous in acid environments and cause severe localized attack once the passive film get broken. This section describes recently patented acid corrosion inhibitors for applications such as in acid pickling and acid cleaning.

Khomyakova *et al.* patented a chemical composition for use in etching of metals and acid treatment of equipment in energetics, food industry etc, that comprises of n-brominebenzal-m-nitroaniline, 2-chlorine-6-diethylamino-4-methyl pyridine, 1,3-bis(carbamoyltio)-2-(N,N-diemethyl-amine) propane hydrochloride, and urotropin. The composition is good for protection of steel, Al and Ni, and also for reduction of steel hydrogenation [44]. Kurochkin *et al.* patented an inhibitor combination of 5-nitro-salycylalsulphathiazole, 3-dodecylbenzimidazole iodide, polyethylene-polyamine; for protection of steel, Ti and Al and also for inhibition of hydrogen pick up [45]. A combination of alpha-oxynaphtalisonicotine hydrazide, 2,4,6-tris(2-isotioureido)-s-triazine hydroiodide, 2-(tiazolyl-4)-benzimidazole and urotropin is disclosed by Kravtsov *et al.*, for steel, Al and In and for reduction of hydrogen charging of steel [46]. Alkarylated polyalkyl pyridinium salts inhibit over pickling of Fe and alloys in HCl/H_2SO_4 pickling baths [47]. Li *et al.* proposed an environment friendly inhibitor used in pickling of carbon steel. The inhibitor contains 1-amino-2-mercapto-5-[1′-(1′,2′,4′-triazole)-methy-lene]-1H-1,3,4-triazole and/or 1-phenyl-2-(5-[1′,2′,3′,5′-tetrazole-methylene]-1,3,4-furodiazole) thioalkyl ethyl ketone [48].

It has been discovered that simple diols (ethylene glycol or propylene glycol) and triols (glycerol) work as corrosion inhibitors in concentrated organic and inorganic acids without any neutralization of the acids. These corrosion inhibitors are cheap and readily available in large quantities. The diols and triols also reduce evaporation of the acid, and thus improve the working environment [49].

CORROSION INHIBITORS IN LUBRICANTS, HYDRAULIC AND METAL WORKING FLUIDS

One of the causes of wear in an internal combustion engine is corrosion of the metal surfaces of the engine. The corrosion promoting compounds present in the crankcase are principally weak organic acids which may result from nitration and oxidation of the lubricating oil due to contamination by blow-by gases and exposure of the lubricant to high temperatures. For the purpose of preventing corrosivity by these compounds on the various engine parts, it is necessary to incorporate dispersants, detergents, and corrosion inhibitors in the lubricating oil composition. It is desirable to minimize the amount of phosphorus in lubricants. Although phosphorus does not contribute to ash, it can lead to poisoning of catalysts.

Boudreau disclosed a lubricant composition containing P and S free organotungstates imparting improved antiwear, corrosion, and antioxidant properties. The organic tungsten complex is a reaction product of a mono- or diglyceride and a tungsten source, or of a secondary amine, a fatty acid derivative and a tungsten source [50]. Corrosion inhibitors such as oil soluble 2,5-dimercapto-l,3,4- thiadiazole or hyd-rocarbyl-substituted 2,5-dimercapto-l,3,4-thiadiazole derivative was used in a patented lubricating composition by Tipton *et al.* [51]. Na or Ca salt of dinonylnaphthalene-sulfonic acid was used as a corrosion inhibitor in vegetable oil based lubricants [52]. A patented phosphorous free additive composition contains a hydrocarbyl-substituted 1,2,4-triaxole corrosion inhibitor [53]. Ivanov *et al.* disclosed an inhibitor composition as additives into motor oils and lubricating cooling liquids that contains a lanthanum oxide, triglycerides of higher carboxylic acids, alkylbenzenesulfonic acid, alkanolamine, lanthanum nitrate and organic solvent in the balance [54].

VAPOR PHASE CORROSION INHIBITORS

Vapor phase (volatile) corrosion inhibitors (VCIs) have the particular advantage that the vaporized molecules can reach hard-to-reach areas commonly found in electronic enclosures, between two metal flanges and similar other systems. The VCI envelop the metal article in a non-corrosive layer and retard moisture and oxygen present in the atmosphere from attacking and reacting with the metal surfaces. VCI may be applied by combining the inhibitor with a liquid and spraying the entire surface of the metal article to be protected. Alternatively, VCI may be incorporated into a packaging material such as paper and plastic wraps, films, and plastic dunnage for the protection of metals from corrosive environments during for example shipment, storage or handling. Different VCIs or combinations of VCIs may be selected based on the type of metal to be protected, the size of the enclosure, and the length of time that protection is required.

Most of the patents in this area are dealing with novel products using the conventional VCIs. A recently patented VCI containing packaging films for metals includes phosphate esters, caprylic and isononanoic acid and amino-2-methyl-1-propanal [55]. Damiani patented an improved skate guard comprising a pouch and a corrosion inhibitor which is useful for protecting the blade of an ice skate during storage and protects the blade of the skate from rusting. A silicone based VCI was employed for the same [56]. Morota *et al.* patented an anticorrosive tri-layer polymer sheet comprising a propylene intermediate layer containing VCI. The steel sheet (JIS G 3141) stored in the polymer container at 50 ^{o}C and relative humidity of 100% for 14 days exhibited complete protection [57]. Lyublinski *et al.* disclosed a rust-resistant tape that comprises a polymer base material layer, an adhesive layer and a rust-resistant component. The rust-resistant component comprises at least one VCI that is placed into the matrix of the polymer base material or the adhesive layer. The rust-resistant tape in accordance with the present invention can be directly applied to a metal surface to be protected [58]. A synergistic corrosion management systems designed to eliminate, manage, control and/or mitigate corrosion in containers, enclosures, cisterns and/or storage tanks utilized a combination of cathodic-based corrosion prevention system, soluble corrosion inhibitor, and VCI [59].

Very high volatility of VCIs is a disadvantage when these compounds are incorporated into organic polymeric materials at high temperatures. Additionally, VCIs must have a high thermal stability. The known VCIs may not satisfy in every respect the high requirements which a corrosion inhibitor is required to meet, especially with regard to incorporation into plastics at high temperature. It has been found that alkylaminosiloxanes based compounds is particularly suitable for use as corrosion inhibitors for protecting metallic surfaces in such applications [60].

One of the issues with current VCI emitting packaging materials is that the inhibitor often can not be seen or detected by close inspection. This creates a number of drawbacks to the use of VCIs. For example, end users of the packaging article do not have a convenient method to confirm that the packaging article contains an appropriate VCI mixture. Unless expensive analytical tests are performed, it is difficult to assure that the vendor incorporated the VCI concentrate or master batch into the articles in the right amounts. It would be highly desirable to provide a simple way of determining whether a given volatile corrosion inhibiting mixture is present in or on an article. Mcconnell disclosed a corrosion inhibiting mixture comprising a carrier, a VCI, and a tracing agent which absorbs light in the ultraviolet region of the electromagnetic spectrum, and re-emits light in the blue region of the electromagnetic spectrum. Particularly significant in this regard is the potential the invention affords for providing a high quality, low cost VCI mixture tracing agent [61].

CORROSION INHIBITORS IN OTHER MAJOR APPLICATIONS

Corrosion Inhibitors in Electronic Industry

Chemical mechanical polishing or planarization (CMP) is a process in which material is removed from a surface of a microelectronic device wafer, and the surface is planarized. In its most rudimentary form, CMP involves applying slurry, e.g., a solution of an abrasive and an active chemistry, to a polishing pad that buffs the surface of a microelectronic device wafer to achieve the removal, planarization, and polishing processes. Many patents are available on CMP solution utilizing corrosion inhibitors [62, 63]. Yoshikawa *et al.* patented a composition for mechanochemical polishing that was comprised of phosphonium salt, triazole based corrosion inhibitor and colloidal silica [64]. Chang *et al.* patented sarcosine and its salts as corrosion inhibitors during cleaning after chemical mechanical polishing [65]. In a patented printed circuit boards with long term reliability consists of corrosion inhibiting layers containing benzotriazole or nitrophenylhydrazine (for metals such as W-Cu, Mo-Cu, Cu etc) in the wiring layers, applied at least on the peripheries of the plating layers [66].

Concrete Corrosion Inhibitors

Tobacco products such as dried tobacco leaves, stems and dust are added to cementations concrete and mortar to inhibit corrosion. The tobacco addition protects steel embedded in Portland cement from corrosive attack. Tobacco is renewable, potentially inexpensive bioproduct that provides excellent corrosion protection with little or no environmental concerns [67]. Imasawa patented an aqueous styrene-butadiene co-polymer emulsion corrosion inhibitor for reinforcing steel for autoclaved lightweight concrete [68]. A 50:50 combination sodium benzoate and alkali metal sebacate was used as a migrating inhibitor (VCI) in the polymer fiber, in post-tensioning cables [69].

Other Applications

Nanoscale inorganic corrosion inhibitors such as nanoscale silica, nanoscale titania, nanoscale zinc oxide, or their mixtures are used in anti-corrosive antibacterial plastic metal composite tube. The composite tube comprises a plastic outer layer (contains 0.2-8% of inhibitor), a plastic inner layer (contains nano Ag), and a metal layer. The inventive plastic metal composite tube has the advantage of good sterilization function on water body, good resistance to aging, long service life and no pollution [70].

Ureido silanes are patented as aqueous corrosion inhibitors [71]. Quraishi *et al.* disclosed a process for preparation of a stable 1-cinnamylidine-3-thiocarbohydrazide, the compound acts as a corrosion inhibitor for mild steel [72]. Biodegradable and non-toxic sodium triethylenetetramine bisdithiocarbamate was patented for corrosion inhibition for Cu in acidic conditions [73].

Many other patents are reported on corrosion inhibitors for various applications such as in batteries [74], in electroless plating [75], in ware washing detergent composition [76], in road deicing applications [77], in coating remover compositions [78] etc. A trace amount of tungstate added together with an ortho-phosphate and/or phosphonite is disclosed for inhibiting corrosion by an ammonium nitrate fertilizer solution in contact with ferrous metal storage tanks and equipment surfaces [79].

CONCLUDING REMARKS

R&D in different areas of corrosion inhibitors is exploring newer methods and products. Recent patents (2008-2009) in the field of corrosion inhibition are reviewed here and are presented according to the area of application of the inhibitors. Conventional inorganic inhibitors continue to be a major component in many patented inhibitor combinations. Few novel inhibitors are introduced. Many of the reports deal with novel inhibition methods in various applications. Few patents explored nanotechnology for better inhibition. Novel packaging products are patented based on VCIs.

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