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A review of corrosion inhibitors for rust preventative fluids

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ABSTRACT

Corrosion of metals has been a widespread issue in industries for centuries. The use of corrosion inhibitors in rust preventative fluids are commonly employed to provide the temporary corrosion protection to metals. The aim of this review is to summarize the rust inhibition properties, inhibition mechanism, chemistry and development of corrosion inhibitors for rust preventative fluids. Some suggestions for further research on corrosion inhibitors have also been discussed.

1. Introduction

Corrosion is the degradation of a material's properties by chemical and/or electrochemical reaction with the environment, and in most cases it means the electrochemical oxidation of metal. The study of National Association of Corrosion Engineers (NACE) estimated that the global cost of corrosion to be $ 2.5 trillion annually, equivalent to about 3.4% of the global Gross Domestic Product (GDP) [1]. It also found that implementing corrosion prevention best practices can save 15–35% of the cost of damage, that is $ 375–875 billion. Among the various methods available to prevent corrosion of metals, rust preventative fluids are extensively used to provide temporary corrosion protection during manufacturing processes, storage and shipment.

Rust preventative fluids are prepared by mixing corrosion inhibitors, film-forming agents and other additives into a base fluid, and it can be classified as solvent-based, oil-based and water-based rust preventatives according to the types of base fluid [2]. It is definite that corrosion inhibitors are critical for them to achieving high performance. Inorganic and organic inhibitors are the two main types of corrosion inhibitors. Inorganic inhibitors, such as nitrite, nitrate, chromate, dichromate, phosphate, are widely used in different base fluids and for various metals [3]. On the other hand, organic inhibitors are the compounds containing one or more polar groups (with O, N, P, S atoms, and π electrons), which are effective to prevent corrosion *via* adsorption on the metal surface [4–6]. Since the polar groups are usually regarded as the reaction centers for the adsorption process, the strength of adsorption is strongly dependent on the electron density and polarizability of the polar groups [7]. Accordingly, organic inhibitors include sulfonates, alcohols, ethers, amines, amides, amine salts, carboxylates, heterocyclic nitrogen compounds, phosphates, polymers, natural products, and others in consideration of polar groups nature. The present article reviews the mechanism and development of corrosion inhibitors for rust preventative fluids.

2. Mechanism

Generally, corrosion is the oxidation of metal through an electrochemical process. In the meanwhile, a reduction occurs at the cathode which can produce either H_2 in acidic system or OH^- in neutral/alkaline system, as shown in Scheme 1. It is clear that corrosion inhibitors can work efficiently by preventing either the oxidation of metal or the reduction. According to the mechanism of corrosion inhibition, corrosion inhibitors can be classified as anodic inhibitors, cathodic inhibitors and mixed inhibitors [8].

As the name suggests, anodic inhibitors can retard the anodic reaction by forming a protective oxide film on the metal surface (Fig. 1), which require a critical concentration for metal protection since they can accelerate corrosion when the concentration is low [8]. There are two action modes: one is the oxidizing inhibitors that can passivate the metal in the absence of oxygen, such as chromates and nitrites. Hexavalent chromium (Cr (VI)) and nitrites are reduced during the process. The other is nonoxidizing anions that require the presence of oxygen to passivate the metal, such as phosphates and silicates. These inhibitors will promote the rapid formation of a protective oxide film on the anodic areas [9].

Cathodic inhibitors act by either slowing down the cathodic reaction or selectively precipitating on cathodic regions to interrupt the flow of electrons from the anode to the cathode (Fig. 1) [10]. Unlike the anodic inhibitors, the cathodic inhibitors are not corrosive even at low concentrations. Typical examples are As_2O_3, zinc sulfate, nickel sulfate.

Mixed inhibitors are organic compounds that adsorb on the metal surface with film formation and prevent both the anodic and cathodic

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Anode:

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

Cathode:

$$2H^+ + 2e^- \longrightarrow H_2 \quad \text{(acidic)}$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad \text{(neutral or alkaline)}$$

Scheme 1. Corrosion reactions on the metal surface.

reactions. As shown in Fig. 2, it is generally accepted that the adsorption (physisorption and/or chemisorption) of organic corrosion inhibitors onto the metal surface through the polar head, while the non-polar tail is oriented and closely packed in a direction vertical to the metal surface, which form a tight film and provide a protective barrier to avoid the attack on the base metal [11]. Meanwhile, the physisorption of hydrocarbon molecules from the basestock by the non-polar tail of the adsorbed inhibitor molecules can increase both the thickness and effectiveness of the hydrophobic barrier to corrosion [4,12]. Thus, the matched chain lengths of inhibitors and base oils are required for superior rust prevention [13].

3. Corrosion inhibitor chemistry

3.1. Nitrites and chromates

Since the first use of sodium nitrite ($NaNO_2$) by Wachter to prevent internal corrosion in pipe lines [14,15], it has been widely used as an effective corrosion inhibitor for aqueous systems, such as metalworking fluids [16]. It is supposed that sodium nitrite can assist the cathodic process and provide the protection with the formation of protective oxide film [17]. Nitrite functions as an oxidizing agent to oxidize iron (II) into iron (III), resulting in the formation of a stable passive film of maghemite (γ-Fe_2O_3) on the metal surface, as shown in Scheme 2 [18–21].

However, sodium nitrite can react with the amines under conditions that commonly used as additives in metalworking lubricants and result in the formation of nitrosamines (Scheme 3), which has been classified as "probably carcinogenic to humans" by International Agency for Research on Cancer (IARC) [22]. Thus, the use of nitrite has been prohibited in cutting fluid containing an ethanol amine salt of a carboxylic acid by the USA Environmental Protection Agency [23].

Chromates, such as potassium dichromate, is another corrosion inhibitor that were used in rust preventatives and lubricants previously.

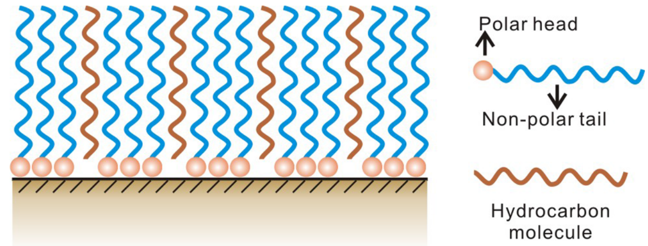


Fig. 2. Schematic mechanism of mixed inhibitors.

$$2Fe^{2+} + 2OH^- + 2NO_2^- \longrightarrow 2NO + \gamma\text{-}Fe_2O_3 + H_2O$$

Scheme 2. Maghemite formation with nitrite.

$$R_2NH + NaNO_2 \longrightarrow R_2N\text{-}N{=}O \text{ (nitrosamine)}$$

Scheme 3. Nitrosamine formation.

Similarly, the hexavalent chromium (Cr (VI)) has been recognized as a human carcinogen, and the use of chromates was also banned in 1990. From viewpoints of safety and environmental protection, nitrites- and/or chromates-containing metalworking fluids are restricted, and there is a great need for environmental friendly water soluble corrosion inhibitors as alternatives, which can provide comparable rust preventative performance to that of solvent-based and oil-based rust preventatives.

3.2. Sulfonates

The petroleum sulfonates began to be used as oil additives in the 1930s, and widely used for rust inhibition during World War II to protect military goods during shipment [24,25]. Currently, metal sulfonates are one of the most extensively used corrosion inhibitors in rust preventative formulations [26–31]. According to the feedstock, they can be divided into petroleum or synthetic sulfonates; while considering the metal cations, they can be classified as Ba, Mg, Ca, or Na salts. Early studies indicated that the adsorption of various sulfonates from anhydrous oil solution was determined by the choice of cations, and the cation size would determine the charge separation and the dipole strength of sulfonate groups [32]. In general, it has been observed that the corrosion inhibition performance of cations increased in the order: Na < Mg < Ca < Ba [24,32]. Among them, barium and calcium sulfonates are widely employed in industrial formulations due

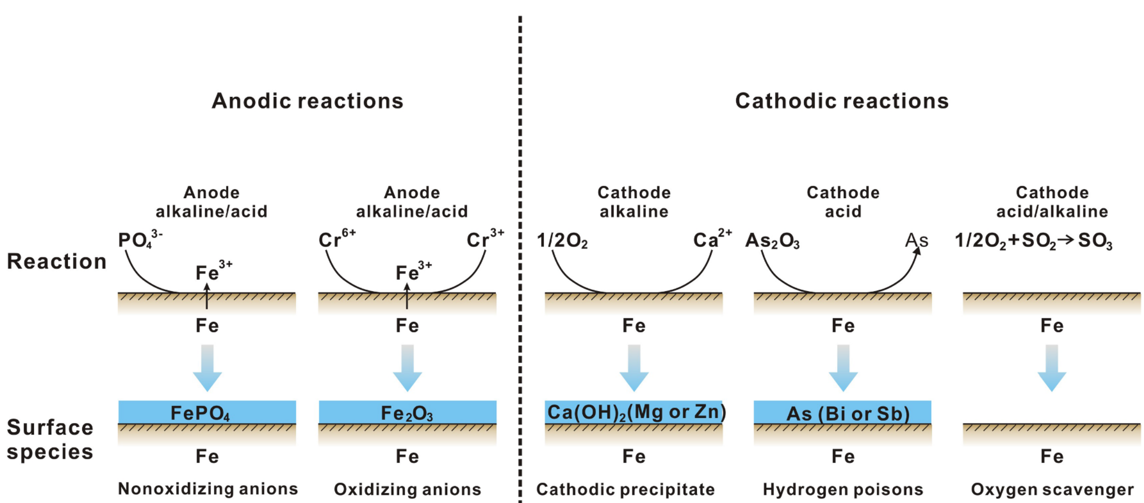


Fig. 1. Schematic mechanism of anodic and cathodic inhibitors [8].

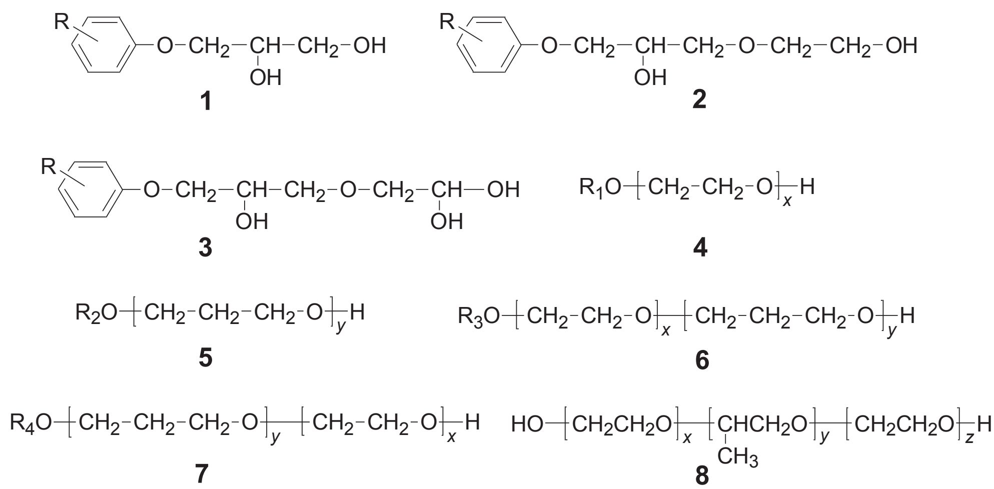


Fig. 3. Alcohol- and ether-based structures.

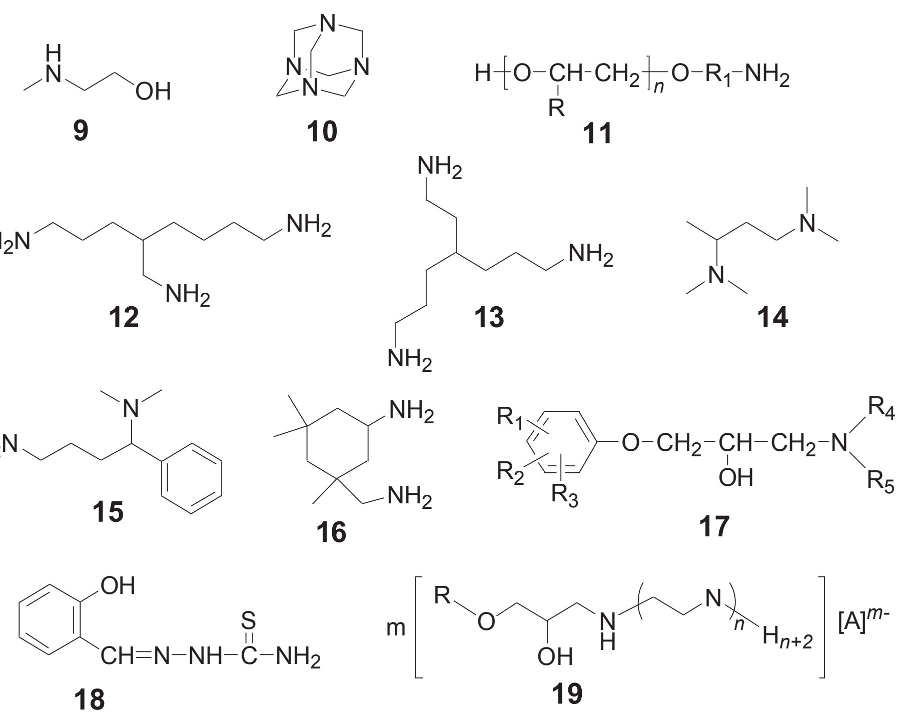


Fig. 4. Amine-based structures.

$$\underset{\textbf{HMT}}{C_6H_{12}N_4} + 4NaNO_2 + 10H_2O \longrightarrow 6HCHO + 4NH_4NO_2 + 4NaOH$$

$$NH_4NO_2 \longrightarrow NH_3 + HNO_2$$

Scheme 4. Decomposition of HMT and sodium nitrite.

to their outstanding rust prevention and water displacement properties, while sodium sulfonates are more applied for making water emulsifiable rust preventives [33]. Since there are some environmental concerns for barium, recently the rust preventive formulations have been more focused on the development of calcium sulfonates-containing compositions to provide equal or even better performance than barium-based products [34]. Not only the neutral salts, but also the overbased calcium sulfonates act as efficient rust preventives in dual roles, where the sulfonates can form the protective film, and the calcium carbonate can neutralize the acidic components which may cause rusting. Nose et al. found that sodium sulfonates would cause brown stain on steel which was identified as Fe_3O_4 and iron sulfonate [35], and another study suggested the stain was caused by water soluble sulfonates and inorganic salts in the sulfonates [36]. The industry has made great efforts to prepare the sulfonates with narrow molecular weight distribution for providing excellent oil stain prevention and rust prevention performance. Although a variety of sulfonates are well developed as very useful corrosion inhibitors, it is still challenging for the sulfonates based complex compositions to achieve extreme salt spray performance while maintain almost invisible film thickness.

3.3. Alcohols and ethers

Although metal sulfonates can provide sufficient rust protection with high concentration, the trend towards low-ash or ashless corrosion inhibitors has attracted wide attention to meet the sulfated ash restrictions. Kimura et al. reported a series of rust inhibitors comprising of glycerol alkyl phenylether (**1–3**, Fig. 3), and the rust preventative composition may

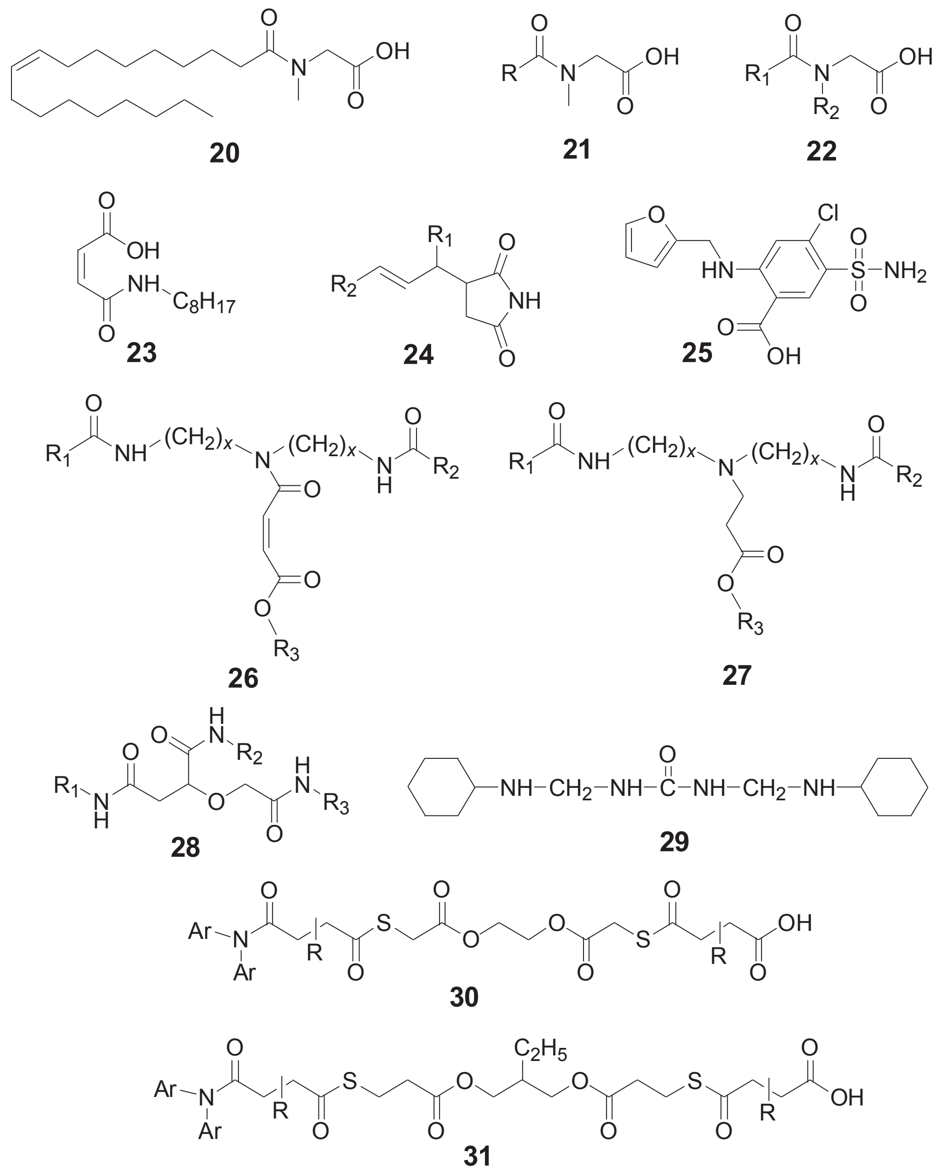


Fig. 5. Amide-based structures.

be obtained by adding the rust inhibitor to a mineral oil [37–39]. Rhodes disclosed the use of ethylene oxide or propylene oxide derivatives (**4–7**) as a supplemental rust inhibitor additive combined with overbased detergent additive in a lubricating oil composition for internal combustion engines, showing superior rust and corrosion inhibition [40]. Emert et al. also disclosed the compositions with the improved rust inhibition properties which comprise the ashless rust inhibitor having the similar structure of polyoxyalkylene polyol or ester (**8**) [41].

3.4. Amines

The amines, such as the alkanolamines including monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA), are well known as corrosion inhibitors in various metalworking fluids and lubricants applications. However, these organic amine type rust inhibitors are still insufficient in rust prevention, and the development of the amine-based compounds with a remarkable rust preventive effect is highly desired [42]. A rust preventive composition comprising an aryl phosphate, a polyolester, a calcium petroleum sulfonate and N-methylethanol amine (**9**, Fig. 4) is effective in protecting metal surfaces by direct or vapor phase contact [43]. Due to their high volatility, the composite vapor phase corrosion inhibitor for aluminum was prepared by the mixture of hexamethylenetetramine (HMT, **10**) and sodium nitrite, and it showed a good rust-inhibiting property when the molar ratio of HMT to sodium nitrite was 1:4. The rust-inhibiting mechanism can be explained as follows: on the one hand, both HMT and sodium nitrite are hygroscopic, and they can prevent corrosion by decreasing the moisture; on the other hand, they will decompose with the water absorbed, as shown in Scheme 4. The decomposition products formaldehyde and nitrous acid can function as reductants to prevent corrosion of aluminum, and ammonia can neutralize the acidic substances in the sealed environment [44].

The reaction product (**11**) of orthoboric acid and alkanoletheramine, which is water soluble, can be used in aqueous solutions to provide excellent corrosion inhibition action without foaming [45]. It has been found that a saturated aliphatic triamine of 9 carbon atoms having at each terminal position a primary amino group and being branched in the 4-position of the main chain, such as 1,3,6-triaminomethylhexane (**12**) and 1,2,3-triaminoethylpropane (**13**), is an effective anti-corrosive agent showing a remarkable rust preventive effect to metals even when used in a small amount [42,46]. Not only the aqueous system, the combination of corrosion inhibitors comprising an oil soluble basic nitrogen compound (**14–16**) and an alkyl or alkenyl

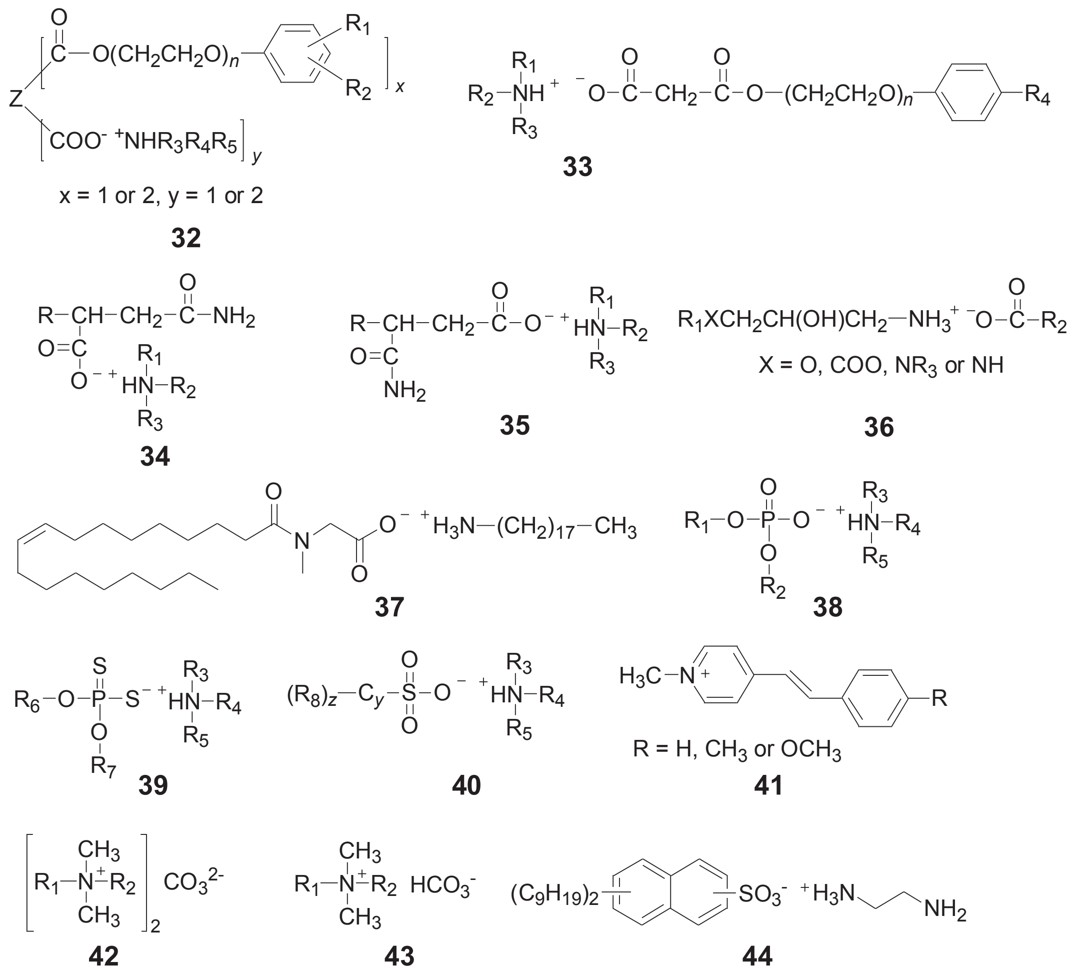


Fig. 6. Amine salt-based structures.

succinic acid are developed for lubricating oils for internal combustion engines [47], and 2-propanol derivatives (**17**) are proposed to possess excellent activity as corrosion inhibitors for lubricants in contact with ferrous metals [48].

A Schiff base, namely N-(2-hydroxybenzylidene) thiosemicarbazide (HBTC, **18**) was investigated as an inhibitor for carbon steel [49,50]. The results indicated that HBTC functioned as a corrosion inhibitor by suppressing both the cathodic and anodic processes *via* adsorption on the metal surface which obeyed the Langmuir's adsorption isotherm. A water soluble rust preventive additive comprising a polyethylene polyamine derivative (**19**) was provided with excellent rust prevention properties, low foaming properties while with little adverse effect on the environment [51]. Since some amines (such as diphenylamine) are commonly used as antioxidants in lubricants, it is absolutely reasonable to assume that the efficient multifunctional additives with anti-oxidation and rust inhibiting properties based on the amine compounds can be well designed and further investigated.

3.5. Amides

For the amides in rust preventative fluids, the high electron density of an amide group will promote adhesion to the electropositive metal surface, while the long hydrocarbon chains will repel against water, resulting in the corrosion inhibition [52,53]. A great many ashless amides have been proposed for rust prevention with more stringent environmental regulations. N-oleoyl sarcosine (**20**, Fig. 5) is one of the oldest amide-based oil soluble rust inhibitors that can be applied in gasoline, mineral oil and silicone lubricants [54]. The following studies indicated a synergistic effect of the mixture of sodium nitrite and N-acyl sarcosines (**21**) as corrosion inhibitors in lubricating greases, and a synergistic rust inhibiting composition consisting of N-acyl sarcosines (**21**) and an amine salt of a dicarboxylic acid [55,56]. For practical applications, the solubility of corrosion inhibitors in both oil and water is desirable. It is reported that an acyl amino acid derivative (**22**) combined with a triazole derivative can provide corrosion inhibition either in organic hydrocarbon or water based system [57].

For water-based cutting fluids, anti-bacterial property is also essential for application. N-alkyl carboxylic acid amide (**23**) was prepared from the reaction of cyclic acid anhydride and fatty amine, showing both good anti-rust and antimicrobial activity [58]. The combination of metallic and ashless rust inhibitors in lubricants yielded improved rust protection and demulsibility, where the metal rust inhibitor is a metal sulfonate and the ashless rust inhibitor is a alkenyl succinimide (**24**) [59]. As the inhibition efficiency is reported to follow the sequence O < N < S [60,61], the sulfur-containing amide furosemide (**25**) can be used as an environmental-friendly corrosion inhibitor for zinc metal in acid medium [62]. Moreover, US4743388A disclosed the fatty acid substituted diamide derivatives (**26**, **27**) showing excellent lubrication and rust inhibition properties for metalworking fluids [63], and the triamide of 2-oxabutane-1,3,4-tricarboxylic acid (**28**) can be used as anti-corrosion agents in lubricants [64].

Not only amides, amide derivatives bis-(cyclohexylaminomethyl)-urea (BCMU, **29**) has been found to be good vapor phase corrosion inhibitors for mild steel [65]. The results suggested that BCMU interacts with the ferric ions *via* N and O atoms in its molecule, and BCMU can stabilize the oxide layer and decrease the surface roughness. With the

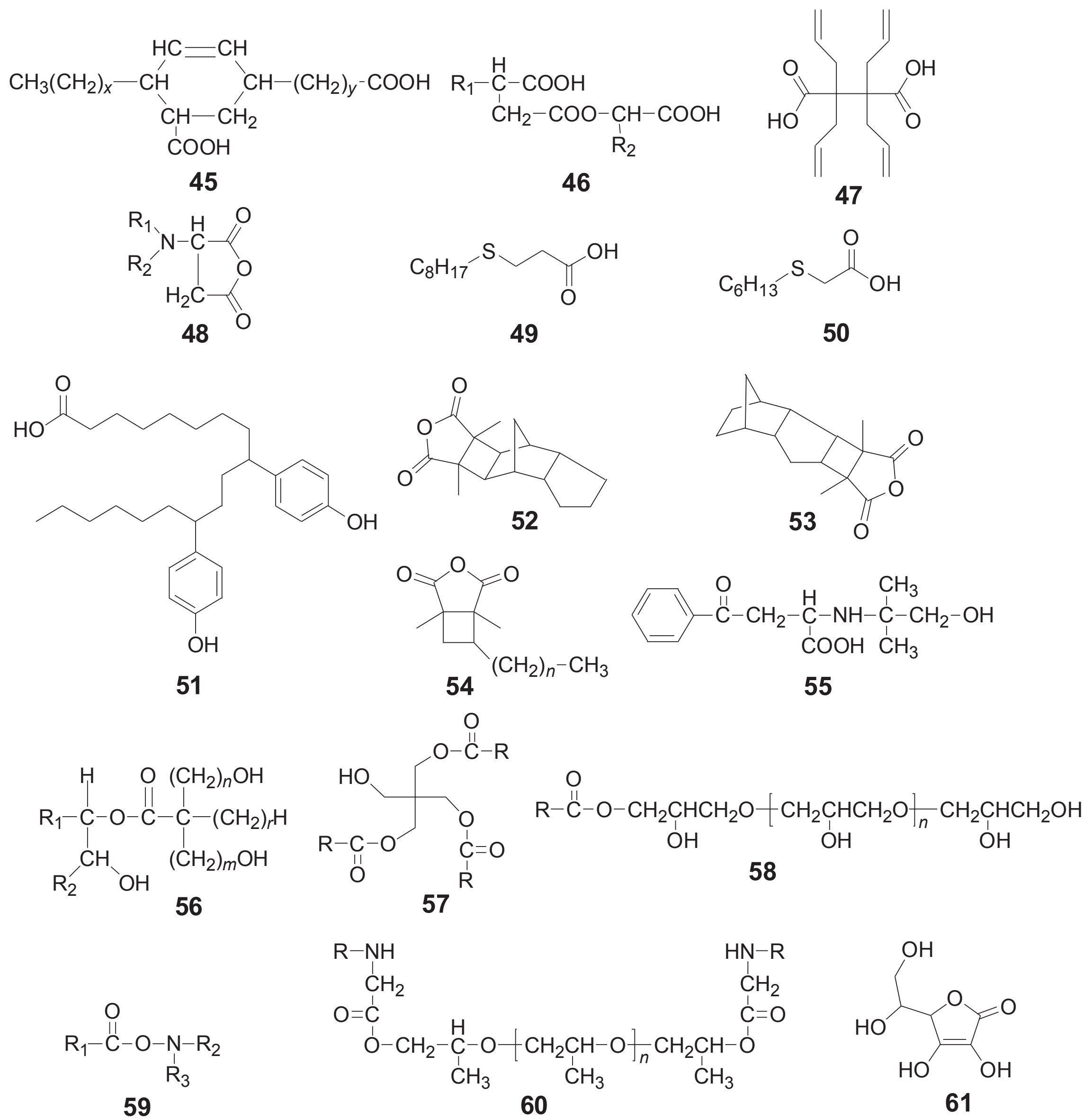


Fig. 7. Carboxylate-based structures-Part 1.

key functional groups synergistically united in the common structure, the product (**30**, **31**) prepared by the reaction of an arylamine with a hydrocarbyl acid anhydride and a thioester can be used as effective multifunctional anti-oxidation, anti-wear, rust inhibiting additive for lubricants and fuel [66].

3.6. Amine salts

Amine salts, especially amine salts of carboxylates, have been used to prevent metal corrosion for many years. They are convenient for use since they are formed *in situ* by the reaction of amine and carboxylic acid. Not only corrosion inhibition, but also the lubricity, emulsification and detergency are provided by the neutralized amine carboxylates in metalworking fluids. It has been understood that there is an effect of the number of carbon atoms on performance, and the carboxylic acids ranging from C18 to C22 are the most qualified candidates, such as tall oil fatty acid (TOFA) neutralized with TEA [67,68]. Moreover, the alkyl ammonium carboxylate salt-ethoxylated alkyl phenol esters of a trimer or dimer acid (**32**, **33**, Fig. 6) are efficient corrosion inhibitors that can be used in hydrocarbon fuel or oil composition [69–71]. To improve the water solubility, alkenylsuccinic acid half-amides (**34**, **35**) can also be used as anti-corrosion agents with low foaming tendency in aqueous solutions [72]. US 4589992A and US 4740331A claimed the new amine salts of carboxylates (**36**) provided excellent corrosion inhibition activity combined with good solubility in non-aqueous function fluids [73,74]. It is interesting that the synergistic effect is observed between barium-free metal sulfonates and the amine salt of N-oleoyl sarcosine with octadecylamine (**37**) [75].

Apart from carboxylic acid, the alkylated amine salt of alkylphosphoric acid (**38**), dialkyldithiophosphoric acid (**39**) or hydrocarbyl aryl sulphnoic acid (**40**) are reported to be used combined with anti-oxidants in lubricating oil compositions [76]. Noor et al. investigated the corrosion and inhibitor adsorption process in mild steel/1-methyl-4[4′(-X)-styryl] pyridinium iodides (**41**)/hydrochloric acid systems [77]. It was found that compounds **41** exhibited a very good performance as corrosion inhibitors for mild steel, and the adsorption of inhibitors on mild steel obeyed the Langmuir adsorption isotherm at all studied temperatures. It also showed that the performance of inhibitors was dependent on the electron donating properties of the substituent, and the inhibition efficiency increased in the order: -H < CH_3 < OCH_3. With both water and oil solubility, it has been discovered that the composition containing quaternary ammonium carbonate or

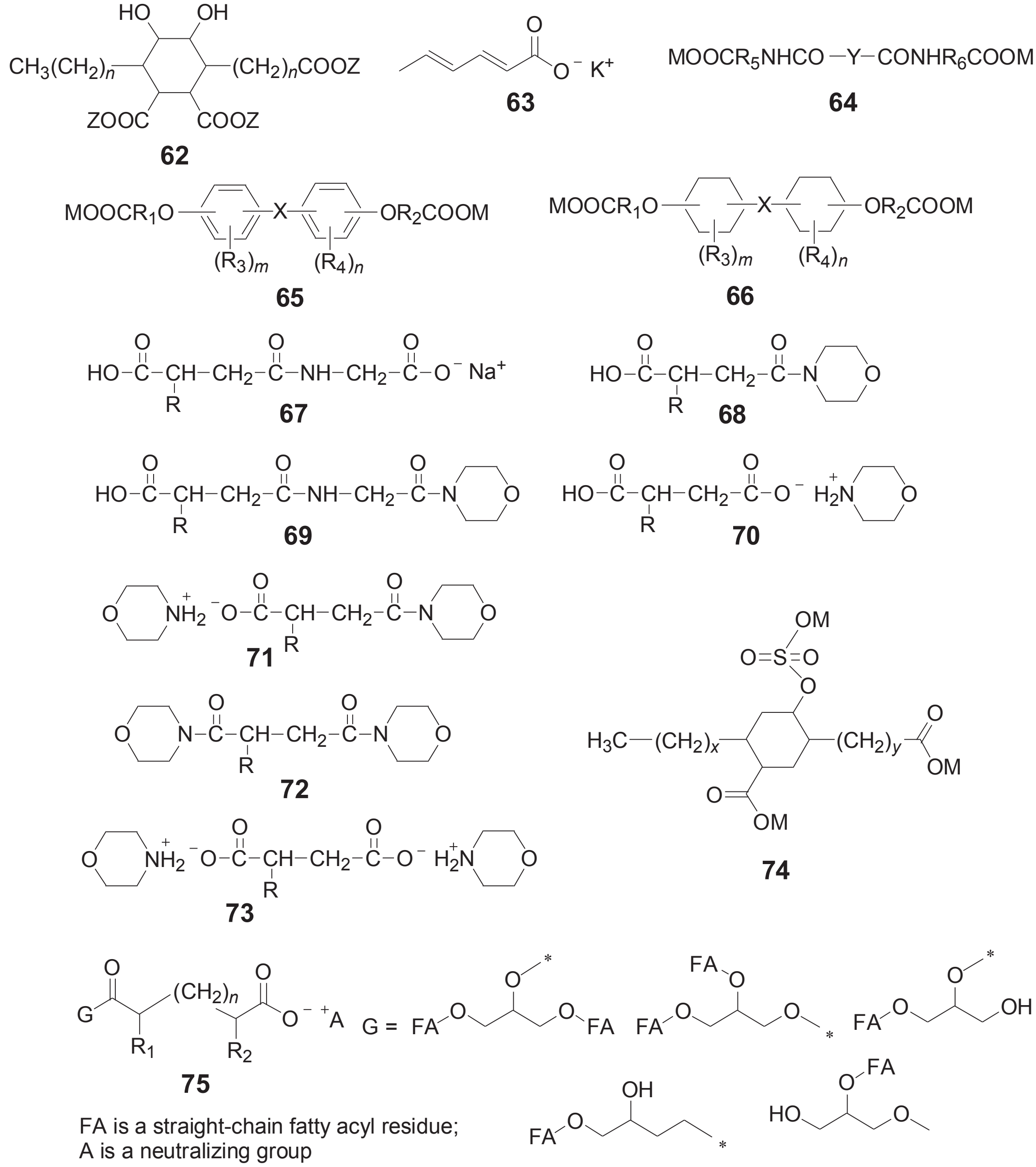


Fig. 8. Carboxylate-based structures-Part 2.

bicarbonate (**42**, **43**) can be used as corrosion inhibitors with additional cleaning capability and antimicrobial protection [78]. To meet the anti-corrosion and extreme pressure anti-wear properties requirements of functional fluids, US 5531911A disclosed the metal free hydraulic fluid with the amine salt of an alkyl-substituted naphthalenesulfonic acid (**44**) possessing good anti-rust and anti-wear performance [79].

3.7. Carboxylates

Carboxylates can provide the corrosion protection with the formation of hydrophobic film by the adsorption of carboxylate group (Lewis base) on the metal surface (Lewis acid) [80–82]. The long-chain fatty acids, such as oleic acid, soya fatty acid, TOFA, and polymerized fatty acids, such as dimer acids, have been well recognized as corrosion inhibitors in various applications, whereas the short-chain fatty acid may promote the corrosion. The use of dicarboxylic acid (**45**, Fig. 7) and dicarboxylic ester-acids (**46**) derivatives as effective additives for preventing corrosion of metals in compositions have been studied [83–86]. A combination of tetra propenyl succinic acid derivate (**47**) and succinic anhydride amine derivatives (**48**) is synergistically effective in reducing rust formation in lubricating oils [87]. However, it should be noted that the dicarboxylic acids have the tendency to precipitate in the presence of Ca^{2+} or Mg^{2+} ions, which would result in a lack of rust prevention property [88]. Kawato et al. investigated a number of derivatives of thiocarboxylic acid prepared from the reaction of 3-mercaptopropionic acid and alkyl halides, and it showed that octylthiopropionic acid (**49**) and hexylthioacetic acid (**50**) possessed excellent anti-corrosion properties for water soluble metalworking fluids and were usable in hard water without precipitation [89]. Besides rust inhibition, multifunctionality is another demand for corrosion inhibitor development. With the introduction of phenol group to long-chain fatty acid, Gisser et al. prepared a series of hydroxyarylstearic acids, and 9,12-bis(4-hydroxyphenyl)stearic acid (**51**) exhibited the most effective combination of antioxidant and rust inhibitor [90,91].

During the last few decades, it has been proposed that the derivatives of carboxylates, including the photo-adducts of dimethylmaleic anhydride and olefins (**52–54**) [92], toluylalanine (**55**) [93], polyhydric ester (**56**) [94], tri-partial esters from pentaerythritol (**57**) [95], polyglycerin fatty acid esters (**58**) [96], amine carboxylate (**59**) [97] and polypropylene oxide dialkylsarcosinates (**60**) [98], are useful

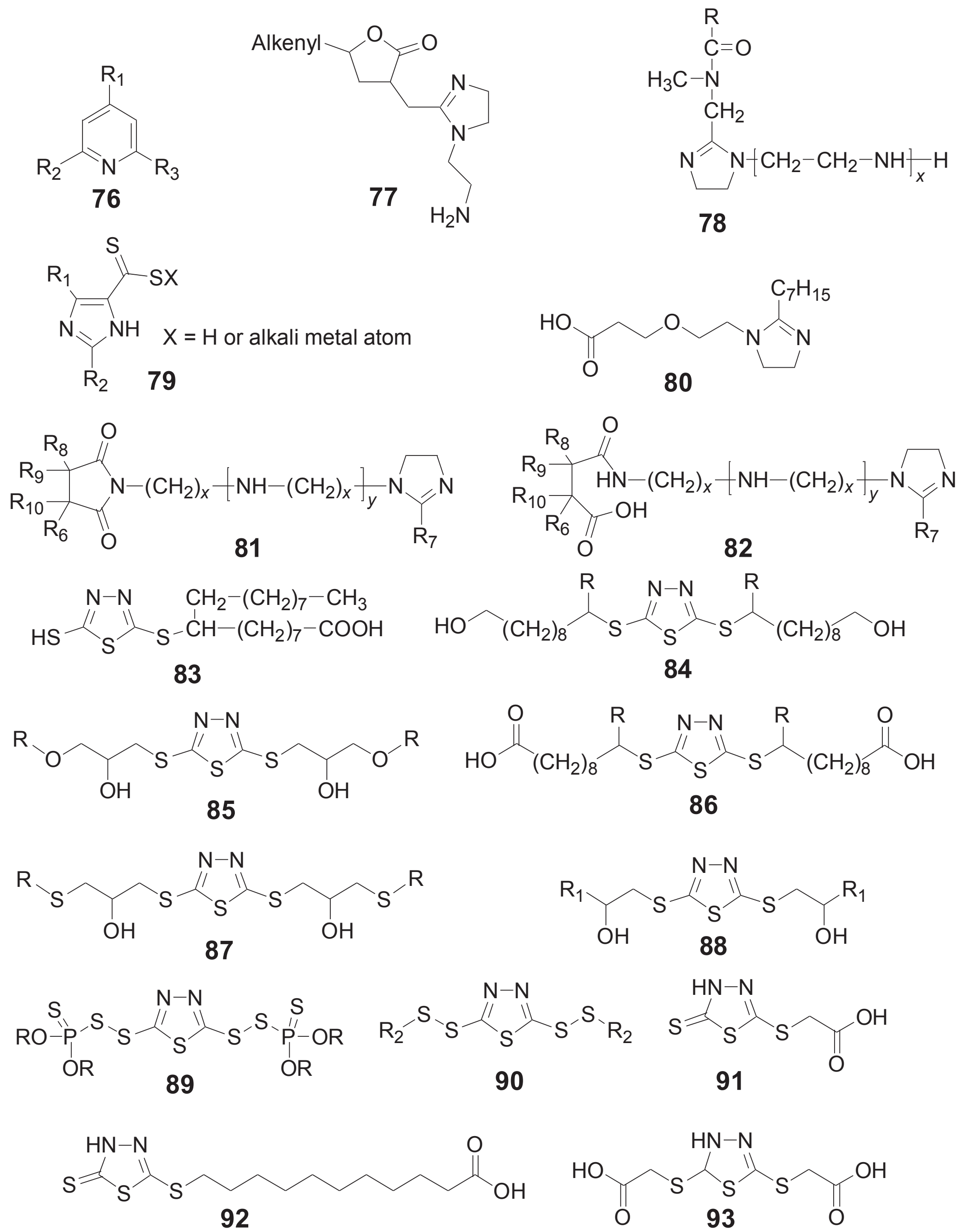


Fig. 9. Heterocyclic nitrogen compound-based structures-Part 1.

corrosion inhibitors with strong rust preventive properties in lubricants and fuels. It is supposed that two or more polar groups in one molecule would be beneficial to rust inhibiting performance [99,100]. With the hydroxy and carboxylate groups in molecule, L-Ascorbic acid (**61**)-Vitamin C is desirable and proved to be a reasonable corrosion inhibitor for mild steel, and the corrosion process is inhibited by the adsorption of the L-dehydroascorbic acid (an oxidation product of L-ascorbic acid) onto the mild steel surface [7].

Followed the study of hydroxycarboxylic acids and esters, carboxylic acid salts have attracted attention. Sodium benzoate (C_6H_5COONa), that is the sodium salt of benzoic acid, is a typical example, which has been shown to be an effective inhibitor for various metals including steel, zin, copper, copper alloys and aluminum alloys [101,102]. It is found that a salt of hydroxycarboxylic acid having a cyclohexane ring (**62**, Fig. 8) provides the excellent rust preventive effect on various metals with the practical advantages of low toxicity, safety and low foaming [103]. Not only for widespread anti-microbial use, the derivatives of sorbic acid, such as potassium sorbate (**63**), can be used as a preventative for rust, corrosion and scale on metal surfaces [104]. US 4466902A disclosed that the carboxylate-based rust inhibitors (**64–66**) have an excellent rust preventing effect for a wide variety of metals, and good chemical stability and anti-oxidation stability due to the basic skeleton of aromatic or alicyclic ring [105]. Then, it is discovered that the reaction products of substituted succinic acid or anhydride with metal hydroxides or amines (**67–73**) [106] and the sulfated dicarboxylic acids derivatives (**74**) [107] can be used as highly effective anti-rust agents for lubricating oils or metalworking fluids, respectively. It is desirable that the organic salts of glyceride-cyclic carboxylic acid anhydride adducts (**75**) derived from renewable resources, such as animal or vegetable oils, can be used as corrosion inhibiting compositions [108]. However, it appears that many esters and carboxylic acid salts will cause the emulsions which is disadvantageous to separating water displaced from metal surface in practical applications.

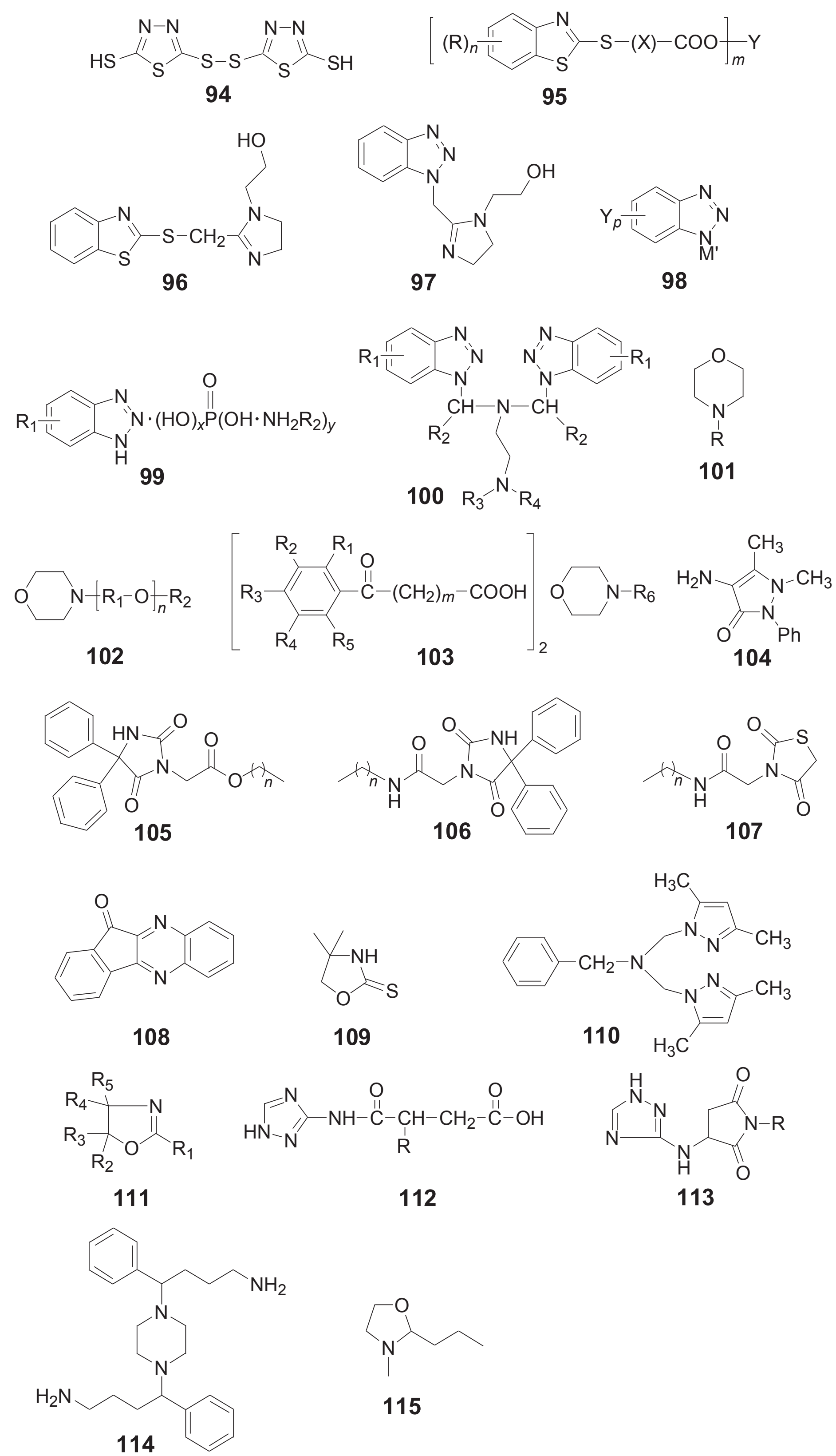
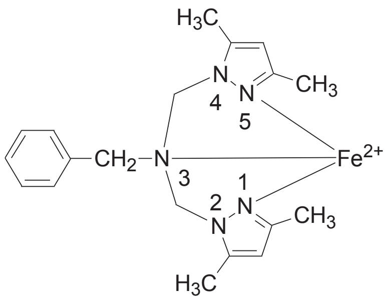


Fig. 10. Heterocyclic nitrogen compound-based structures-Part 2.



Scheme 5. Complex formed on the steel surface by **110** [111].

3.8. Heterocyclic nitrogen compounds

Many heterocyclic nitrogen compounds, such as imidazolines, thiazoles, triazoles, benzotriazoles and pyrazoles, have been proved to be effective ashless corrosion inhibitors for many metals [109,110]. They can adsorb on the metal surface, block the active sites on the surface by the bond formed between the N electron pair and/or the π electron cloud and the metal, and thereby reduce the corrosion [111]. The rust inhibiting and demulsibility performance of a lubricating oil can be synergistically enhanced by a rust inhibitor containing at least one carboxylic acid and a particular class of pyridine derivatives (**76**, Fig. 9) [112]. Different with pyridine, imidazoline-based inhibitors consist of a five-atom ring with two nitrogen atoms in the structure, which will somehow affect the inhibition performance combined with the long hydrocarbon chain attached. The imidazoline derivatives (**77–82**) are reported to be excellent corrosion inhibitors for many metals, and the inhibition efficiency and mechanism have been investigated [113–119]. In addition to the well-known extreme pressure and anti-wear properties provided by mercapto- and dimercapto-thiadiazoles, Gemmill and Wei et al. investigated the anti-corrosion behavior of some derivatives of 2,5-dimercapto-1,3,4-thiadiaxole (**83–90**), respectively, and it appears that the comprehensive performance is dependent on both the type and the structure of the chains attached to the carbon atoms in the 2 and 5 positions of the thiadiazole ring [120,121]. Similarly, Wang et al. studied the tribological, anti-corrosion and anti-rust properties of 2,5-dimercapto-1,3,4-thiadiazole derivatives (**91–94**), and it showed that they can be used as multi-functional additives in the water-glycol hydraulic fluid or lubricant grease additives [122,123].

With the thiazole ring attached to a benzene ring, the presence of heteroatoms (such as N, S, O) and π electrons on the heterocyclic scaffold of benzothiazole derivatives plays the vital role in the corrosion inhibition properties. US 4568753A disclosed that the benzothiazole-substituted carboxylic acids and their salts (**95**, Fig. 10) exhibited rust preventive capability much greater than that of conventional carboxylic acids, and were stably effective with iron, copper and their alloys [124]. Based on the design of N-containing heterocyclic species and imidazoline group combined in an additive molecule, two kinds of compounds (**96–97**) were synthesized and they showed good anti-corrosion, extreme pressure and anti-wear properties [125]. A stable adsorption film can be formed on the metal surface by the coordination bonds between the large π bonds in the molecules with the empty *d*-orbital in metal atoms, and resulting in the good anti-rust and anti-corrosion properties in water-glycol. Although the exact mechanism remains unconfirmed, it is surprisingly discovered that a synergistic corrosion inhibiting effect was provided by the combination of one amido acid or salt and an arytriazole derivative (**98**) in the aqueous metalworking fluid compositions [126]. Furthermore, a triazole adduct of amine phosphates (**99**) and a alkylamine substituted benzotriazole (**100**) can be used as a multifunctional additives for industrial lubricants with improved oxidation stability and rust preventative performance [127,128].

As a low boiling amine, morpholine has been used as a vapor phase corrosion inhibitor, and the investigation on morpholine derivatives (**101–103**) had proved that they are also efficient corrosion inhibitors in fluids for protecting metal surface [129–131]. El-Rehim et al. reported that 4-aminoantipyrine (**104**) behaves as an anodic inhibitor for mild steel, and the polar functional groups in the molecule, such as amine, methylamine, carbonyl and π electron bonds, would effectively contribute to the inhibition of mild steel corrosion [132]. Öztürk et al. synthesized a series of five membered heterocyclic compounds (**105–107**), and the results showed that they were all excellent corrosion inhibitors in mineral oil medium [133]. The aromatic rings in the structures of **105** and **106** can increase adsorption and consequently enhance inhibition efficiency with their π electrons. Obot et al. and Musa et al. reported that quinoxaline derivative (**108**) and 4,4-dimethyloxazolidine-2-thione (**109**) are effective corrosion inhibitors for

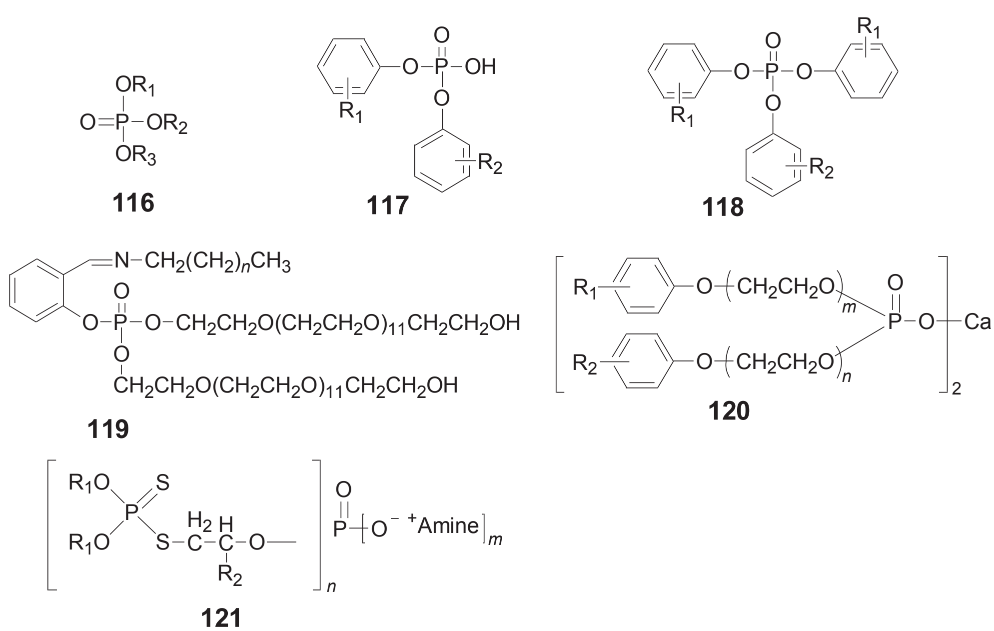
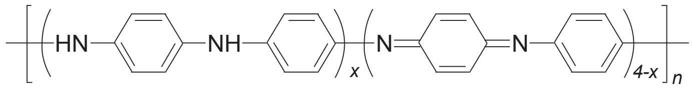


Fig. 11. Phosphate-based structures.



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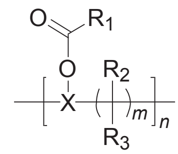

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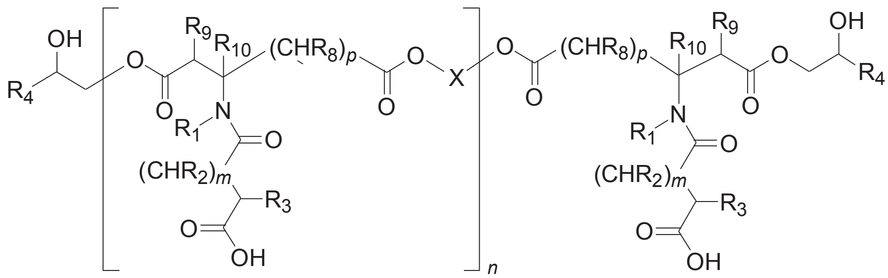
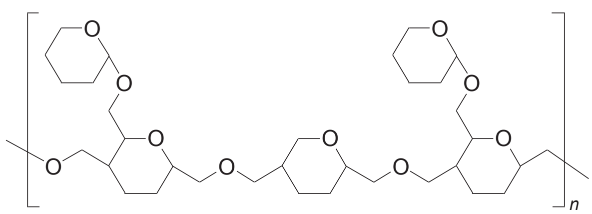
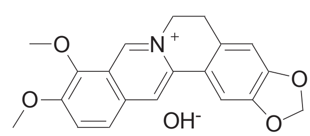


124

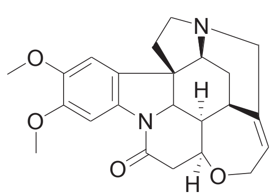
Fig. 12. Polymer-based structures.



125



126



127

Fig. 13. Natural product-based structures.

mild steel, respectively [134,135]. Quantum chemical calculations show that both **108** and **109** molecules can adsorb as molecular species using nitrogen, sulfur, oxygen and the π electrons of the aromatic ring as its active centers. Tebbji et al. studied the inhibition effect of a bipyrazole derivative (**110**) on the corrosion of steel [111]. The high inhibition efficiency of **110** are probably due to the presence of nitrogen atoms, π electrons of pyrazole and phenyl rings and methyl. The nitrogen atoms are the major adsorption centers with the metal surface, as shown in Scheme 5. On the one hand, ferrous ion is surrounded by two pyrazolyl nitrogen atoms at Fe-N (1) and Fe-N (5); on the other hand, bonding may also occur from Fe to amine N (3). Some other heterocyclic nitrogen compounds (**111–115**) have also been investigated as corrosion inhibitors in fuel and lubricating oil compositions [47,136–138]. Due to the high degree of structural diversity they offered, the design, synthesis, property and application of heterocyclic nitrogen compounds as advanced corrosion inhibitors will still be one of the most fascinating research topics in the field.

3.9. Phosphates

Phosphate coating is usually applied to carbon steel, low-alloy steel and cast iron as a pretreatment converting the metal surface to the protective layer of insoluble crystalline iron phosphate for lubricity and corrosion protection [139,140]. Thus, it is reasonable to assume that phosphate is probably a potential corrosion inhibitors in rust preventative compositions. The rust preventive compositions containing an aryl phosphate ester (**116**, Fig. 11), an oil soluble calcium sulfonate and a liquid polyolester are provided to protect both ferrous and non-ferrous metals [141]. Likewise, mixtures of alkylaromatic secondary phosphate (**117**) and tertiary phosphate (**118**) esters can be used as rust inhibiting additives with solubility in hydrocarbon fluids [142]. Hegazy et al. reported that phosphate-based nonionic surfactants (**119**) are effective corrosion inhibitors for carbon steel, and their adsorption on the metal surface obeys a Langmuir isotherm and represents a mixed physical and chemical adsorption [143]. To solve the insufficient solubility of film-forming agents (such as wax, a lanolin fatty acid derivative) in hydrocarbon solvents, an organic phosphoric ester calcium salt (**120**) is used together with a specific amount of water, which can be applied in the rust preventatives with a high solubility in an organic medium, and achieved excellent film formation and rustproof performance [144]. Oil soluble phosphorus- and nitrogen-containing compound (**121**) can be used as multifunctional additives in lubricating oils with improvement of limited slip properties, anti-wear/extreme pressure properties, and corrosion inhibiting properties [145,146].

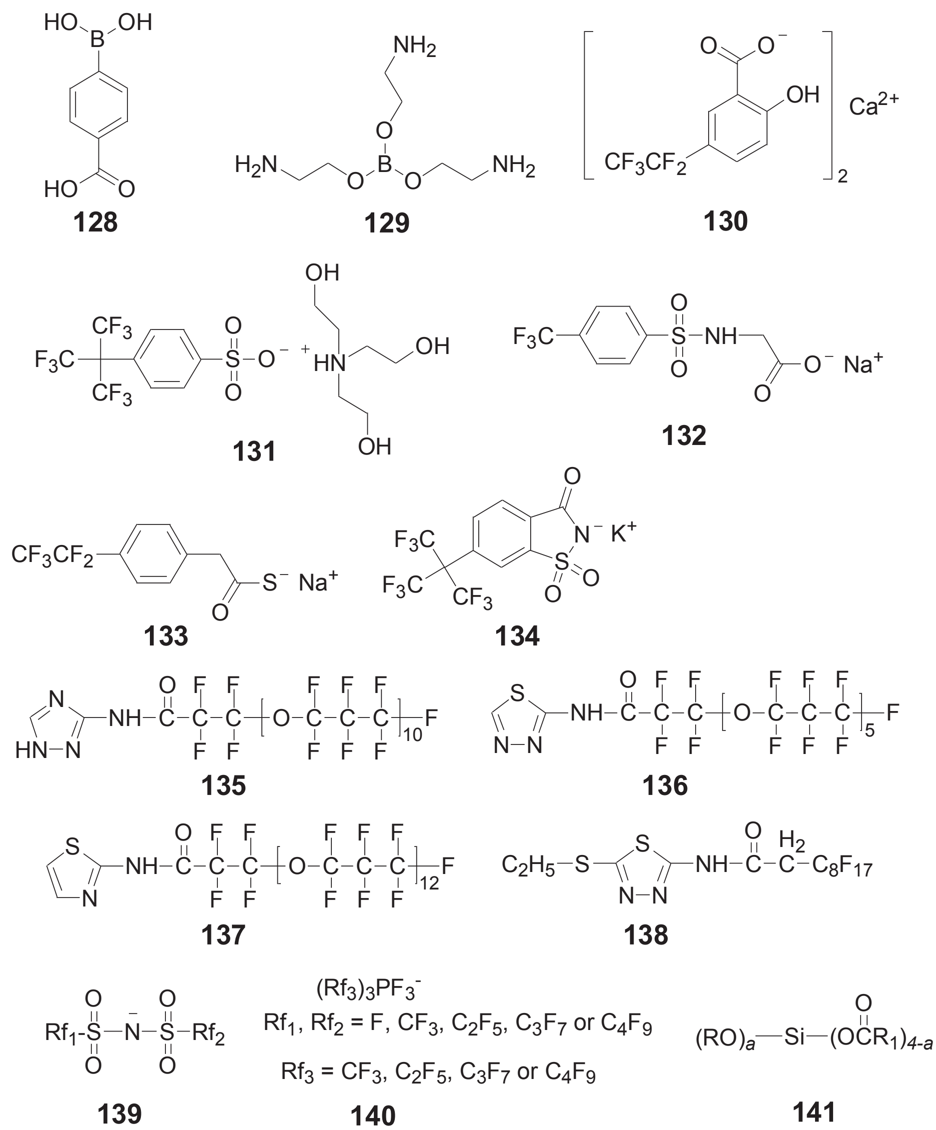


Fig. 14. Other-based structures.

Although phosphate-based corrosion inhibitors have been extensively used, there are growing concerns about their long term toxicity and negative environmental impact.

3.10. Polymers

Some studies indicated that organic polymers having multiple adsorptive polar groups may also act as effective corrosion inhibitors. It is reported that the oil soluble sulfonated aliphatic hydrocarbon polyolefin polymers neutralized with a metal compound, ammonia, ammonium salt or amine, are capable to improve the viscosity, dispersancy, varnish inhibition, detergency and anti-rust properties [147,148]. Polyaniline (**122**, Fig. 12) was first used for metal corrosion prevention since 1985 [149]. Recently, Zhang et al. reported that the rust preventive oil containing an oil soluble polyaniline together with lanolin or lanolin soap provided good rust prevention effect, especially outstanding salt spray resistance [150]. Besides, both polymers **123** and **124** can be used as rust inhibitors in formulated industrial lubricants [151,152].

3.11. Natural products

Although there are large numbers of synthetic compounds that can be used with excellent corrosion inhibition activity, most of these compounds are not only expensive but also toxic to both human beings and environment. Thus, there has been considerable interest in the development of novel corrosion inhibitors from natural products which are environmental friendly, non-toxic, biodegradable and readily available [153,154].

Tannins, which is a class of non-toxic, environmental friendly and biodegradable polyphenolic compounds extracted from plants, have been used for corrosion protection since 1936 [155] and can be applied as green corrosion inhibitors for steel and alloys in aqueous solutions, especially in acidic electrolytes [156–163]. The adsorptive behavior of tannins at $pH < 3$ is probably due to the chemisorption of tannin molecules on the metal surface; while at $pH \geq 3$, the inhibition is probably due to the physisorption of ferric tannate that formed on the metal surface [156,157,160]. A synergistic inhibition behavior is observed by the blends of tannin and calcium gluconate in the near neutral media [164]. The addition of calcium gluconate in tannin solutions increases the pH of solutions and ensures the formation of low soluble protective iron tannate and metal gluconate on the metal surface.

Guar gum (**125**, Fig. 13), a polysaccharide compound extracted from guar beans, can act as a corrosion inhibitor for carbon steel due to the horizontal adsorption on steel surface [165]. Berberine (**126**), an alkaloid that can be abstracted from natural *coptis chinensis*, can act as an effective green corrosion inhibitor for mild steel [166]. The density distribution of highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) indicated that there are several adsorbed sites in one molecular, resulting in strong adsorption and high inhibition efficiency. Brucine (**127**), the major alkaloidal constituent isolated from *Strychnos nux-vomica*, can act as a good inhibitor for steel, and the coordination of the hetero atom with metal surface is revealed by IR analysis [167]. Many studies indicated that *Solanum tuberosum* [168], *Citrus aurantiifolia* leaves extract [169,170] and nanosilicate extraction from rice husk ash [171] can be used as green corrosion inhibitors for steel.

3.12. Others

In addition to the above mentioned corrosion inhibitor chemistry, there are still some other types of corrosion inhibitors, as shown in Fig. 14. During the past few decades, much effort has been devoted to developing borates as lubricant additives since they possess anti-wear, friction-reducing and anti-oxidation characteristics [172–175], while the research on rust inhibition performance of borates is limited. 4-Carboxyphenylboronic acid (**128**) has been found to be an efficient carbon dioxide corrosion inhibitor for steel in aqueous medium [176]. A synergistic inhibition effect has been found when they are combined with amines, that is the borated amines. The aqueous cutting fluid containing a reaction product of boric acid with TEA provides superior protection of ferrous metals against corrosion, which is currently being widely used in aqueous rust preventive compositions [177]. Dermawan et al. found that the use of boron-containing additives (**129**) prepared by reacting boric acid with MEA can improve the rust prevention performance of the bio-based lubricating oils [178].

Fluorine-containing compounds, including fluorosilicone, polyfluorochloroethylene, polyfluoroalkyl polyether (PFPE), having excellent thermal and oxidative stabilities, have been extensively applied in lubricants that are used under high vacuum and high temperature conditions, such as space lubricating oils [179,180]. The aromatic- and fluorine-containing compounds (**130–134**) can effectively prevent corrosion of various metals [181,182]. Dekura developed the corrosion inhibited synthetic lubricants comprised of fluorine- and heterocyclic-containing compounds (**135–138**) with enhanced adsorption on metals, resulting in outstanding anti-corrosion properties [183]. Ionic liquids based on fluorine-containing anions (**139** and **140**) can be used in a lubricant composition and exhibit excellent rust prevention properties, which can be applied under a high vacuum or under high temperatures [184].

Moreover, oil soluble tetra-functional hydrolysable silane compounds (**141**) are used to a lubricating oil composition for internal combustion engine to improve copper corrosion performance [185]. Although nanoparticles and nanocomposites have been introduced in coatings for corrosion prevention and water repellency, there are only few studies available on the role of nanotechnology in rust preventative fluids [186–188]. The composition including an effective amount of charged cellulose nanocrystals in stabilized aqueous suspension can be used for inhibiting corrosion of metals, such as steel [189,190].

4. Conclusions and prospects

Rust preventative fluids are widely used in industry to provide the temporary corrosion protection to metals during manufacturing processes, storage and shipment, and the corrosion inhibitors used in rust preventative fluids are critical to regulating their rust inhibition performance. The inhibition mechanism, chemistry and development of corrosion inhibitors for rust preventative fluids are summarized. Since many conventional corrosion inhibitors are toxic and environmental harmful, the key driving force for corrosion inhibitors development is the non-toxic and environmental friendly corrosion inhibitors. The following directions deserve more attention in future research:

(1) Water is an attractive base fluid since it is inexpensive and has no VOC content, however, the performance for water-based rust preventatives is limited and only effective for short-term indoor protection. Accordingly, there is a significant demand for developing novel water soluble corrosion inhibitors with superior rust preventive performance.
(2) The screening of heterocyclic nitrogen compounds with polar groups and/or π electrons as advanced corrosion inhibitors should be continued.
(3) The development of high efficient multifunctional additives with anti-oxidation, anti-wear, extreme pressure and rust inhibiting properties is the general trend, and the combined mechanisms of action should be investigated.
(4) In consideration of increasing safety and environmental issues, the development of effective, non-toxic and environmental friendly corrosion inhibitors from natural products and bio-based resources is necessary.
(5) Few nanoparticles are introduced in coatings for water repellency and better inhibition, the role of nanotechnology in rust preventative fluids need to be further explored.

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