REVIEW PAPER

Cutting fluid corrosion inhibitors from inorganic to organic: Progress and applications

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(Received 31 August 2021 • Revised 24 November 2021 • Accepted 29 December 2021)

Abstract−Water-based cutting fluid has a broad application area and a hundred year history, but its poor corrosion inhibition and anti-rust ability limit its further promotion. Adding corrosion inhibitors can effectively solve the above problems. However, no review papers are available on cutting fluid corrosion inhibitors, and their mechanism, suitability, and performance influencing factors have not been revealed. This article discusses cutting fluid corrosion inhibitors to fill the gaps in theoretical research and industrial applications. Inorganic matters are initially used in corrosion inhibition due to their strong oxidizing properties. Therefore, the film formation mechanism of inorganic corrosion inhibitor oxide and precipitation film is first analyzed, and the applications in corrosive medium are summarized. Given that inorganic corrosion inhibitors are not environmentally friendly and expensive, organic corrosion inhibitors are currently used as replacement. Thus, the film formation mechanism of different organic corrosion inhibitors adsorption film is analyzed, and their suitability with metals is determined. The influence of molecular structure and temperature on their corrosion inhibition effect is also studied, and the performance of inorganic and organic corrosion inhibitors is compared. However, single organic corrosion inhibitors are greatly affected by metal surface state, temperature, and immersion time. Therefore, the synergistic film formation after the compounding of organic and inorganic corrosion inhibitors is analyzed. In addition, the influence rate of concentration, molecular structure, and temperature on corrosion inhibition performance is revealed, and a matching database of corrosion inhibitor type and metal type in cutting is established. Finally, in view of the limitations of cutting fluid corrosion inhibitors, the establishment of a molecular dynamics model of corrosion inhibitor failure and accelerates corrosion and the development of general-purpose green additives based on the molecular design and physical and chemical analysis of the suitability of corrosion inhibitor and base liquid are prospected.

Keywords: Cutting Fluid Corrosion Inhibitor Inorganic Organic Metal Suitability

INTRODUCTION

1. Overview of Metal Cutting Process and Cutting Fluid

The machinery manufacturing industry is the cornerstone of a country's economic development [1]. Metal cutting is to cut (or grind) the excess metal on the workpiece with a tool (or friction tool) by using a specific amount of power and movement provided by the machine tool [2,3] to obtain a workpiece that meets the required shape, accuracy, and surface quality [4].

Cutting fluid is an important material in industrial production (Fig. 1) [5] that lubricates, inhibits corrosion, enhances heat exchange, ensures machining accuracy and processed parts' surface quality [6], prolongs tool life [7,8], and protects the workpiece [9,10]. This material is generally composed of base oil and various super-func-

Fig. 1. Jet-liquid machining.

tional additives prepared using a step-by-step scientific compounding method. Cutting fluid additives are chemical substances crucial in maintaining and improving the various properties of cutting fluid [6].

2. Classification and Characteristics of Metal Cutting Fluids

Cutting fluids are divided into oil- and water-based [11]. Water-based metal cutting fluids are used after diluting the original liquid with water [12] and can be further classified as emulsions, semi-synthetic, and synthetic [6]. The characteristics of oil- and water-based cutting fluids are shown in Table 1.

Metal processing is gradually transitioning from traditional metal materials such as steel and iron to new metal materials such as aluminum, magnesium, titanium, nickel, and multi-metal composite materials [14]. Some difficult-to-process materials used in heavy-duty processing [15], such as special die steel, stainless steel, high-temperature alloy steel, nickel alloy, titanium alloy, and aviation aluminum alloy, are increasingly applied in metal processing [16,17]. Table 1 shows that compared with traditional oil-based cutting fluids, water-based cutting fluids have better cooling and heat exchange effects [18,19] and are more suitable for the processing of difficult-to-cut materials [20,21] due to the high temperature and pressure requirements of the cutting process [22]. This material is the current mainstream trend of application and research in the field of cutting fluids [23,24].

3. Electrochemistry Corrosion

Except for a few heavy metals (such as gold, platinum, and silver), most metals and alloys have a fatal disadvantage--their insta-bility. A metal reacts electrochemically with the substances in the medium to produce corrosion, a reaction that is spontaneous and irreversible. Especially during metal cutting, the surface of the processed workpiece is fresh, has high chemical activity, and is prone to oxidation and corrosion. Cutting fluid-induced corrosion during cutting mainly includes the following aspects [25].

3-1. OH^- Corrosion

The pH of almost all cutting fluids works within the alkaline pH of 8.0-11.0 [26]. Alkaline media corrode metals. One example is aluminum. First, the protective film Al_2O_3 on the aluminum surface is dissolved in alkaline solution as shown in formula (1).

$$Al_2O_3 + 2OH^- \rightarrow 2AlO_2^- + H_2O \tag{1}$$

The matrix aluminum then combines with OH^- to form AlO_2^-, and hydrogen evolution corrosion occurs as shown in formula (2) [27].

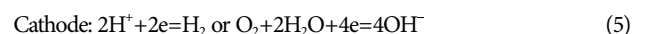$$2Al + 2OH^- + 2H_2O \rightarrow 2AlO_2^- + 3H_2\uparrow \tag{2}$$
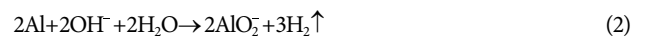
3-2. H_2O and H^+ Corrosion

Water-based cutting fluid is prepared by diluting the original liquid with water at a high amount [6]. During machining with water-based cutting fluid, water molecular liquid gets adsorbed on the newly machined metal surface, and a thin water film is formed on the metal surface. A layer of dielectric solution necessary for electrochemical corrosion is generated when the water film reaches a certain thickness (20-30 molecular layers) [28]. An example is iron.

At anode, iron loses electrons, forms Fe^{2+}, Fe^{2+} enters the water film, and combines with anions in the water film to form complex metal salts, resulting in metal corrosion.

At cathode, under acidic conditions, H^+ in the water film obtains electrons from the cathode and is released as H_2. Under neutral or alkaline conditions, the oxygen dissolved in the water film on the metal surface obtains electrons from the cathode to form OH^-, and the electrode reaction is shown in formulas (3)-(6) [29,30].
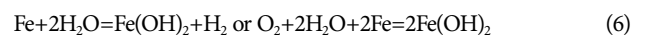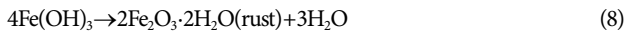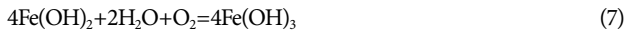
$$\text{Anode: } Fe - 2e = F^{2+} \tag{3}$$

$$Fe^{2+} + 2OH^- = Fe(OH) \tag{4}$$

$$\text{Cathode: } 2H^+ + 2e = H_2 \text{ or } O_2 + 2H_2O + 4e = 4OH^- \tag{5}$$

Total reaction formula:
$$Fe + 2H_2O = Fe(OH)_2 + H_2 \text{ or } O_2 + 2H_2O + 2Fe = 2Fe(OH)_2 \tag{6}$$

Table 1. Performance comparison of oil- and water-based cutting fluids [11,13]

	Oil-based	Emulsions	Semi-synthetic	Synthetic
Component	Base oil+additives	Base oil+additives+water	Base oil+additives+water	Additives+water
Base oil	Mineral oil Vegetable oil Synthetic oil	Mineral oil Vegetable oil Synthetic oil	Mineral oil Vegetable oil Synthetic oil	None
Aspect	Oily	Milky	Translucent	Transparent
Lubricity	Excellent	Good	Good	Poor
Corrosion inhibition	Excellent	Poor	Good	Good
Cooling	Low	Good	Good	Excellent
Fire Hazard	High	Low	Low	Low

$Fe(OH)_2$ is further oxidized to $Fe(OH)_3$, and finally $Fe(OH)_3$ becomes rust as shown in formulas (7)-(8).

$$4Fe(OH)_2 + 2H_2O + O_2 = 4Fe(OH)_3 \qquad (7)$$

$$4Fe(OH)_3 \rightarrow 2Fe_2O_3 \cdot 2H_2O(rust) + 3H_2O \qquad (8)$$
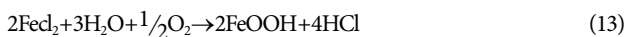
3-3. Atmospheric Corrosion

After machining, a workpiece may be stored for a short time while waiting for the next process, and most stored workpieces are exposed to the air. In addition to the atmosphere basic composition (H_2O, O_2, and CO_2), atmosphere impurities vary in different geographical environments, such as SO_2 in industrial areas and Cl^- and HCl in coastal areas. After machining, a cutting fluid water film forms on the workpiece surface with high humidity. Above atmosphere, pollutants are easily soluble in water and produce electrochemical corrosion to the metal. The corrosion mechanisms are shown in formulas (9)-(15) (with iron as example) [28,31].
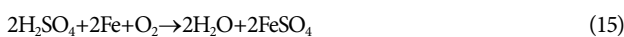
(1) CO_2 corrosion

$$Co_2 \rightarrow Co_2 + H_2O \leftrightarrow HCO_3^- + H^+ \qquad (9)$$

$$Fe^{2+} + 2HCO_3^- + H_2O = Fe(OH)_2 \downarrow + H_2O + CO_2 \uparrow \qquad (10)$$

$$4Fe(OH)_3 \rightarrow 2Fe_2O_3 \cdot 2H_2O(rust) + 3H_2O \qquad (11)$$

(2) HCl corrosion

$$Fe + 2HCl + \tfrac{1}{2}O_2 \rightarrow Fecl_2 + H_2O \qquad (12)$$

$$2Fecl_2 + 3H_2O + \tfrac{1}{2}O_2 \rightarrow 2FeOOH + 4HCl \qquad (13)$$

(3) SO_2 corrosion

$$SO_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow H_2SO_4 \qquad (14)$$

$$2H_2SO_4 + 2Fe + O_2 \rightarrow 2H_2O + 2FeSO_4 \qquad (15)$$
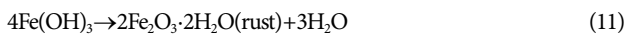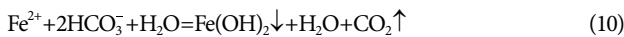
In addition to electrochemical corrosion, corrosion can be caused by the deterioration of cutting fluid [32], improper process treatment handling, and poor state of metal surface [33]. This problem causes direct or indirect economic losses and major safety hazards and accidents [34]. Delaying metal corrosion has always been a topic of widespread concern in industry and academia. During machining, a protective film that can isolate the metal matrix and corrosive medium is formed on the metal surface to effectively solve the above problems. Among the developed technologies, adding corrosion inhibitor is a simple, low-cost, and widely applicable method to inhibit metal corrosion [25]. Due to the film-forming properties of corrosion inhibitors, they can also enhance the lubricating performance of the cutting fluid [35], improve the tool feed rate [36], ensure workpiece production quality [37] and enhance the stability of cutting fluid to a certain extent [38].

4. Corrosion Inhibitor Concept

A corrosion inhibitor is a chemical substance or a mixture of several chemical substances that exists in the environment (medium) in an appropriate concentration producing a corrosion inhibition film on the metal surface to prevent or slow metal corrosion [33, 39] as shown in Fig. 2.

5. Classification of Corrosion Inhibitors

5-1. Classification by Molecular Type

(1) Inorganic corrosion inhibitors mainly include nitrite, chro-
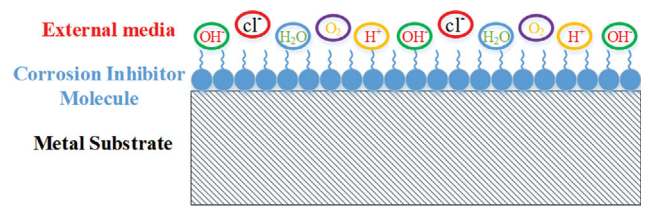

Fig. 2. Mechanism of corrosion inhibitor [6].

mate, zinc salt, molybdate, tungstate, and other oxidizing inorganic substances.

(2) Organic corrosion inhibitors mainly organic compounds with heteroatoms (phosphorus, sulfur, nitrogen and oxygen) and π bonds [25].

5-2. Classification by Effect on Electrode

(1) Anode corrosion inhibitor

Anode corrosion inhibitors can either interact with metal ions in the anode area of a metal surface to form an oxide or hydroxide protective film or use the reduction products generated during oxidation-reduction to fill and repair the original passive oxide film defects on the metal surface. These materials are also called dangerous corrosion inhibitors and must be used in sufficient quantities; otherwise, the battery with large cathodes and small anodes will intensify metal corrosion. At present, corrosion and rust inhibition experiments under different boundary conditions are the only reliable method to determine the quantities of anode corrosion inhibitors [40].

(2) Cathodic corrosion inhibitor

Cathodic corrosion inhibitors can negatively shift the metal corrosion potential and form a precipitation film to slow cathodic corrosion. At insufficient amounts, these materials will not accelerate corrosion at the least and therefore are also called safe corrosion inhibitors. Some examples are zinc carbonate, phosphate and hydroxide, and calcium carbonate [41].

(3) Mixed type corrosion inhibitor

Mixed corrosion inhibitors can form a film on the anode and cathode and can inhibit both their corrosion reaction processes. Although the corrosion potential does not change drastically, the corrosion current is greatly reduced [42,43].

5-3. Classification by Film Forming Mechanism

(1) Absorption film type corrosion inhibitors have hydrophobic and hydrophilic groups in molecules. The latter is in contact with the water molecule, and the former is in contact with the metal, thus forming a protective film with thickness of approximately 1-600 nm [44-46] on the metal surface as shown in Fig. 3(a).

(2) Oxidation (passivation) film type corrosion inhibitors are mainly formed by inorganic corrosion inhibitors, and the thickness of the oxide inhibition film is generally 5×10^3-10×10^3 nm as shown in Fig. 3(b) [47,48].

(3) Precipitation film type corrosion inhibitors alone or with metal ions can have a chemical reaction to produce certain metal precipitates or complexes attached to the substrate surface to form protective film with thickness of approximately 10-100 nm. However, the formed film is not directly bonded to the metal surface and therefore is porous and loose with relatively poor adsorption capacity and lower corrosion inhibition effect than oxide film and
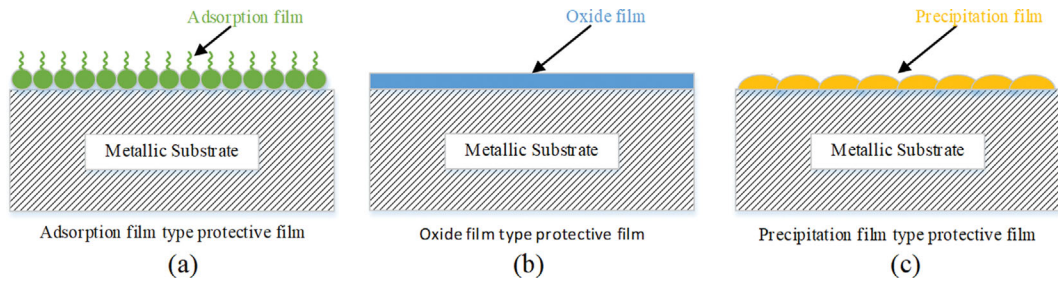
Fig. 3. Schematic of different types of corrosion protection films [6,33].
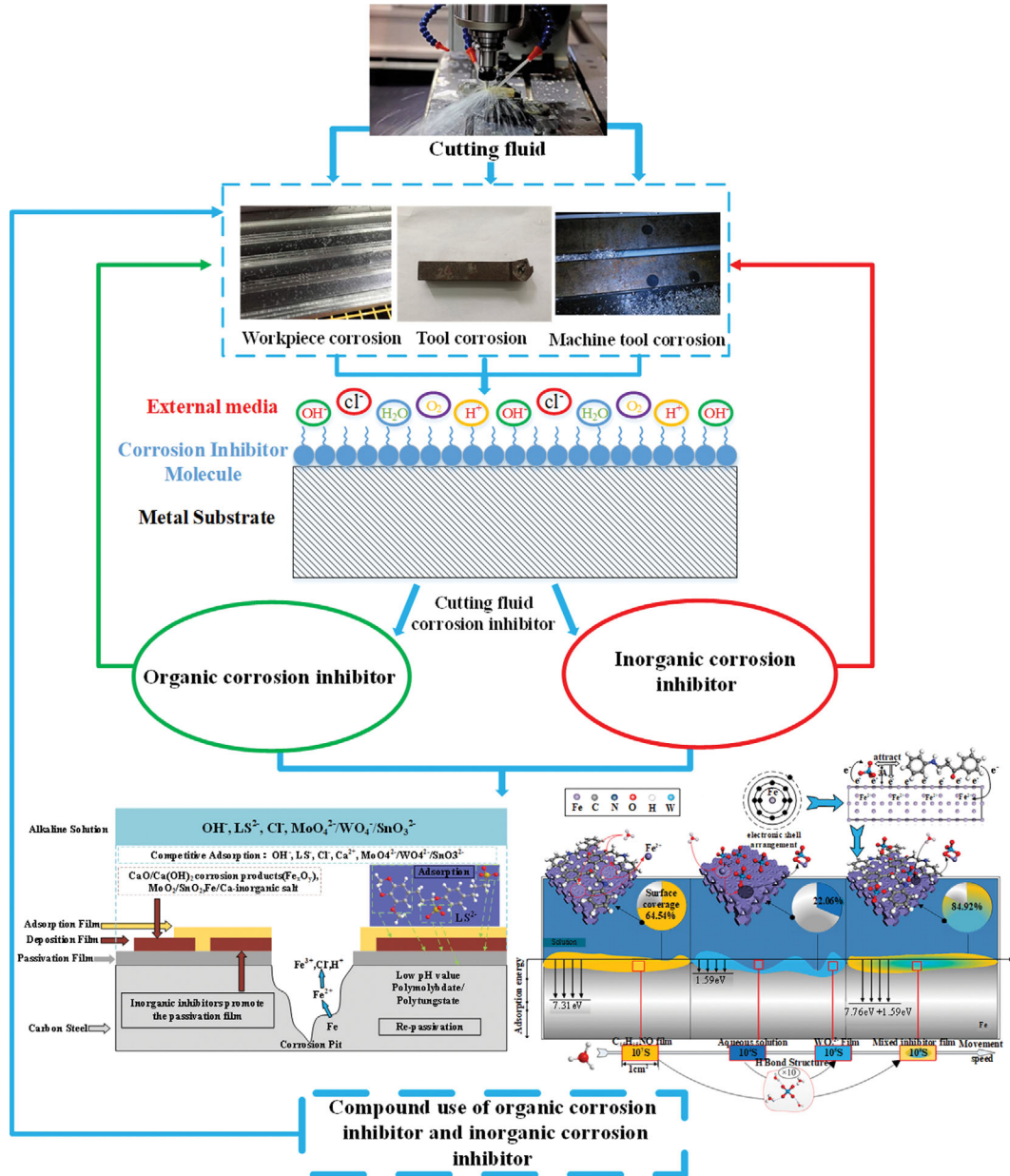

Fig. 4. Article structure.

adsorption film corrosion inhibitors [49] as shown in Fig. 3(c).

Organic inhibitors are generally mixed type inhibitors that generate an adsorption film. Most inorganic inhibitors are anode inhibitors and generally form an oxidation film.

6. Purpose of the Article

Water-based cutting fluid has good cooling and heat exchange

effects and is the main object of application and research in the cutting fluids. However, these substances have high water content (≥92%) and will corrode workpieces and tools. Adding corrosion inhibitor can effectively solve the above problems. The article reviews cutting fluid corrosion inhibitors in order from inorganic to organic. Inorganic matters were first used in corrosion inhibition field due to their strong oxidizing properties. First, the film formation mechanism of the inorganic corrosion inhibitor oxide film and precipitation film is analyzed, and the applications in corrosive medium are summarized. However, inorganic corrosion inhibitors are expensive and not environmentally friendly and thus are currently being replaced with organic corrosion inhibitors. Therefore, the film formation mechanism of different organic corrosion inhibitors adsorption film and their suitability with metals are analyzed. The influence of molecular structure and temperature on the corrosion inhibition effect is also studied, and the performance of different types of inorganic and organic corrosion inhibitors is compared from the perspectives of corrosion inhibition performance, environmental protection, and economy. After the organic corrosion inhibitor and inorganic corrosion inhibitor are compounded, the film formation phenomenon of the synergistic composite film based on the Filling Principle is examined to improve the stability and performance of organic corrosion inhibitors. Conclusions are drawn through analysis, and the development prospects of cutting fluid corrosion inhibitors are presented to provide references for further research and engineering applications of cutting fluid corrosion inhibitors. The article structure is shown in Fig. 4.

INORGANIC CORROSION INHIBITORS

Inorganic corrosion inhibitors are oxidants that promote metal passivation or inorganic salts that form a deposited film on the metal surface. Most inorganic corrosion inhibitors mainly achieve the corrosion inhibition effect by inhibiting anodic polarization. Typical inorganic examples include nitrite, chromate, zinc salt, phos-
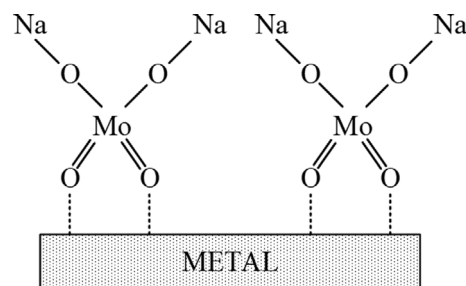

Fig. 5. Inhibition mechanism of sodium molybdate [58].

phate, molybdate, tungstate, and silicate [49,50]. Among them, the use of nitrite [51], chromate [52], and zinc salt [53] has been restricted because they are harmful to the environment and humans. Phosphate leads to eutrophication [54]. The research and application of inorganic corrosion inhibitors are mainly concentrated in molybdate, tungstate, and silicate corrosion inhibitors.

1. Molybdate

Molybdenum belongs to the VIIB group; despite being a heavy metal, its toxicity is 1,000 times lower than that of chromate, a low-toxic compound [55]. This material has a corrosion inhibition effect on black and non-ferrous metals and can be used under acidic and alkaline conditions [50].

The principle of molybdate corrosion inhibition is relatively complicated. In most corrosion systems, the molybdate follows an adsorption mechanism. Molybdate anions (MoO_4^{2-}) react with metal ions to form an oxide film that is attached to the metal surface, is insoluble in the medium, and prevents metal corrosion [56,57] as shown in Fig. 5.

Molybdate anions (MoO_4^{2-}) can be adsorbed on the metal surface and the defects of its self-passivation film to further improve the corrosion inhibition effect [59].

Two views on the mechanism of molybdate adsorb on the metal surface self-passivation film have been presented. One viewpoint is
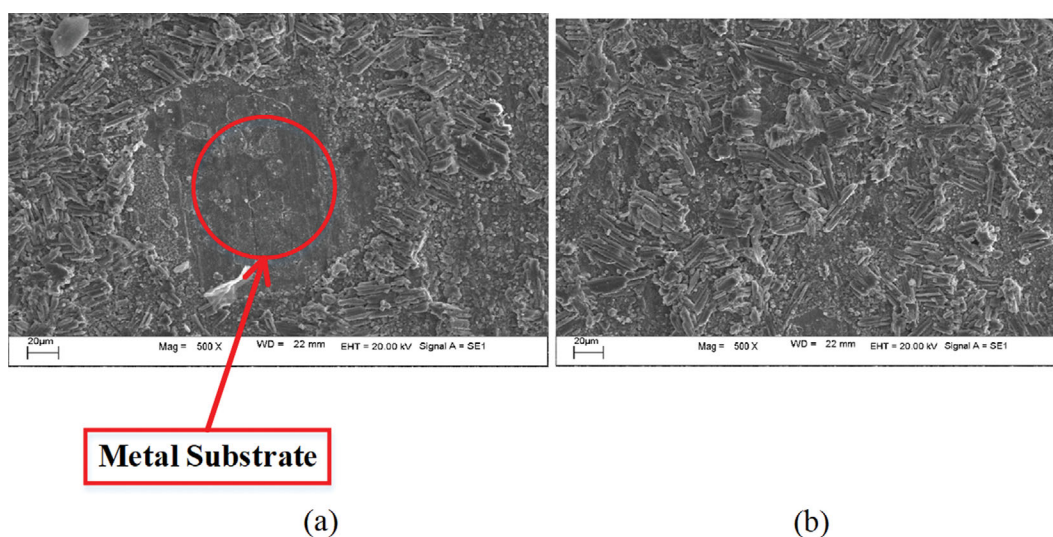

Fig. 6. Surface morphology of Q235 samples immersed in 0.04 and 0.06 mmol/L Na₂MoO₄ solutions for 5 h: (a) 0.04 and (b) 0.06 mmol/L [62].

that molybdate anions (MoO_4^{2-}) and corrosive ions are competitively adsorbed at the defects of self-passivation film, thus weakening the adsorption of corrosive ions and improving the corrosion resistance of the passive film [60]. The other viewpoint is that molybdate anions (MoO_4^{2-}) exhibit induced adsorption on the self-passivation of metal surface, that is, the metal surface passive film is destroyed by the action of corrosive ions, leading to the enhanced adsorption of MoO_4^{2-} on the fresh metal surface where the passive film is broken, thereby inhibiting the development of corrosion to a certain extent [61].

Molybdate is an anodic passivation-type corrosion inhibitor. The passivation film formed at insufficient concentration is incomplete, and some metal substrates can even be observed [62], as shown in Fig. 6. When the concentration does not reach a certain level, this material will even accelerate corrosion, and its critical concentration is high [63]. However, the corrosion inhibition effect of molybdate does not necessarily increase with its concentration. Under special circumstances, the oxidation of a single molybdate on the metal surface is not uniform and thus cannot inhibit corrosion [64].

Molybdate has a particularly outstanding corrosion inhibition effect on cast iron. At low concentration (0.013%) [65] or alkaline environment [66], sodium molybdate has a greater effective corrosion inhibition effect than nitrite and thus is an ideal substitute. Its corrosion inhibition efficiency decreases with the increase in temperature [67], and adding sodium molybdate to cutting fluid can effectively inhibit the leaching of tungsten and cobalt in cemented carbide tools [68].

Sodium molybdate is the most widely used and studied molybdate corrosion inhibitor. The recent applications of sodium molybdate in the different corrosive mediums are summarized in Table 2.

Molybdate is better than nitrite but not as good as tungstate (which is costlier than molybdate) in inhibiting pitting corrosion in alkaline solution. Its oxidizing property is not as good as that of chromate; hence, the compactness of molybdate corrosion inhibitor film is poor. When used alone, the corrosion inhibition effect is of molybdate weaker than that of chromate [66]. Therefore, molybdate is generally used in combination with other corrosion inhibitors, especially organic corrosion inhibitors.

2. Tungstate

Tungsten, chromium, and molybdenum are all VIIB group elements. Tungstate as a metal corrosion inhibitor is similar to chromate and molybdate, but its compounds are almost non-toxic and thus belong to green corrosion inhibitors [75]. When tungstate is
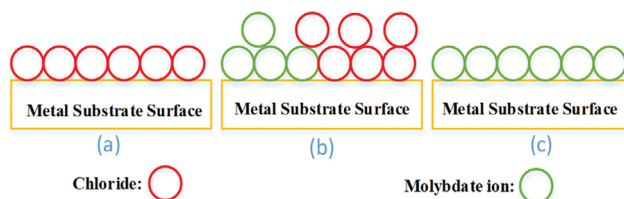

Fig. 7. Schematic of ion adsorption in 3.5% NaCl solution with different molybdate concentrations [77].

added in a corrosive medium, WO_4^{2-} is prone to the polymerization reaction to form $[W_7O_{24}]^{6-}$, $[W_{10}O_{32}]^{4-}$, and other polytungsten anions [76]. These anions and WO_4^{2-} compete with the corrosive ions adsorbed on the sample/medium interface. On the one hand, they weaken the adsorption of corrosive ions on the metal surface. On the other hand, they form an insoluble protective film with the metal ions to isolate the corrosive ions [77] as shown in Fig. 7.

Polytungsten anions and WO_4^{2-} can react with metal ions produced by corrosion to form polytungstate $[Mg^{2+}...WO_4^{2-}]$, which can fill the gaps and repair the defects of the passive protective film, has a strong protective effect on the metal substrate and is expressed as an anode-type corrosion inhibitor [78].

Similar to molybdate corrosion inhibitor, the tungstate corrosion inhibitor is also a dangerous type of corrosion inhibitor. When its concentration does not reach a certain level, this material will accelerate corrosion; however, high-concentration failures have also occurred under special circumstances [29].

Sodium tungstate (Na_2WO_4) is the most widely used and studied tungstate corrosion inhibitor. Its recent applications in the different corrosive mediums are summarized in Table 3.

Molybdate and tungstate corrosion inhibitors are currently expensive [85], dangerous, and require a relatively large dosage. The poor economy is the main factor limiting its large-scale industrial application.

3. Silicate

Silicate has good water solubility and is suitable for preparing water-based corrosion inhibitors. This material can form a protective film on the metal surface. Silicate is inexpensive, non-toxic, and harmless, does not produce harmful substances, and is a good substitute for nitric acid and chromic acid corrosion inhibitors [86].
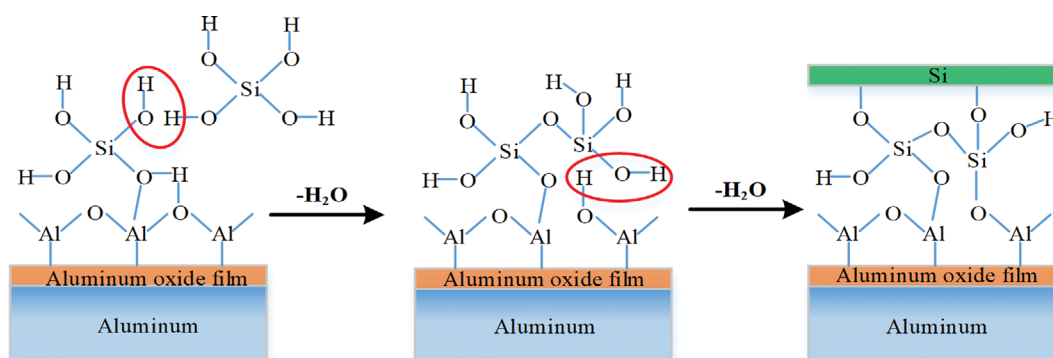
Silicate corrosion inhibitor has a particularly protective effect for aluminum that is better than that of molybdate [87]. Sodium silicate is hydrolyzed into a compound containing Si-OH groups in

Table 2. Applications of sodium molybdate corrosion inhibitor

Reference	Corrosive medium (Solution)	Protected objects	Optimum content	Corrosion inhibition rate
Tommaselli [65]	$Ca(OH)_2+H_2SO_4+HNO_3$ (PH=8)	Carbon steel	0.04%	80%
Tan [69]	Saturated $Ca(OH)_2+0.5$ M NaCl (PH=12.5)	Carbon steel	2,882.84 mg/L	97%
Zhou [70]	0.01 M NaCl+0.1 M $NaHCO_3$ (PH=8.16)	Carbon steel	2,059.2 mg/L	97.9%
Bensabra [71]	Saturated $Ca(OH)_2+0.5$ M NaCl (PH=12.5)	Carbon steel	51,479.3 mg/L	95.9%
Wang [72]	Saturated $Ca(OH)_2+0.5$ M NaCl (PH=12.5)	Aluminum material	2,059.2 mg/L	95.89%
YEE [73]	$Cl^-+HCO_3^-+SO_4^{2-}+CO_3^-+Na^++Ca^{2+}$ (PH=8)	Carbon steel	400 mg/L	98.5%
Wang [74]	30% $(CH_2OH)_2$ (PH=6.5-8.5)	Cast iron	1,000 mg/L	78.2%

Table 3. Applications of sodium tungstate corrosion inhibitor

| Reference	Corrosive medium (Solution)	Protected objects	Optimum content	Corrosion inhibition rate
Subedi [79]	0.5 M NaCl (PH≈7)	Cr-5Ni-53W alloy	>2,400 mg/L	>90%
Gaber [78]	10% H_2SO_4 (PH<1)	Iron-based alloys	$33×10^3$ mg/L	97%
Javidi [80]	3.5% NaCl (PH≈7)	Stainless steel	824.6 mg/L	71.9%
Deepak [81]	1 M NaOH (PH=14)	Carbon steel	800 mg/L	73%
Gao [82]	Saturated $Ca(OH)_2$+0.5 M NaCl (PH=12.5)	Steel	$16.5×10^3$ mg/L	93.3%
Huang [83]	3.5% NaCl (PH≈7)	Carbon steel	1,800 mg/L	80%
Zhang [84]	Natural seawater (PH≈8.0-8.5)	Mild steel	1,000 mg/L	81.3%

Fig. 8. Corrosion inhibition mechanism of silicate corrosion inhibitor [89].

the medium, then undergoes dehydration with the M-OH group on the surface of the metal (M) matrix to form a stable Si-OM bond, passes through the intermolecular cross-linking (the Si-OH groups between the two molecules undergo condensation reaction to form Si-O-Si bonds), and finally forms a dense precipitation film on the metal surface to inhibit aluminum material pitting corrosion and reduce cracks [88] as shown in Fig. 8.

Sodium silicate is the most widely used and researched silicate corrosion inhibitor [90]. These solutions have a relatively complex solution structure and contain monomers SiO_2 and various forms of siloxane polymers. Their composition and distribution in the solution are affected by process parameters such as solution concentration, the molar ratio of SiO_2:Na_2O, and solution aging time; the corrosion resistance is optimal when the SiO_2:Na_2O molar ratio is 2-3.50 [88].

In low-concentration sodium silicate solution, silicate cannot quickly form a complete protective film, and the inhibitory effect is not substantial; thus, the big cathode and small anode effect cause corrosion preferably in the active sites of the substrate [86]. In addition, the corrosive ions continue to wash away the non-compact precipitation layer, thus causing the precipitation layer to fall off and exposing the new metal substrate. These two aspects work together to accelerate metal corrosion. Sodium silicate only exhibits a protective effect on the metal when its content is higher than the threshold [91].

When the concentration of silicate in the solution increases, the polymerization degree of corrosion inhibitor molecules also increases, and monomers condense at high concentrations to form dimers, trimers, oligomers, and higher aggregates as shown in Fig.
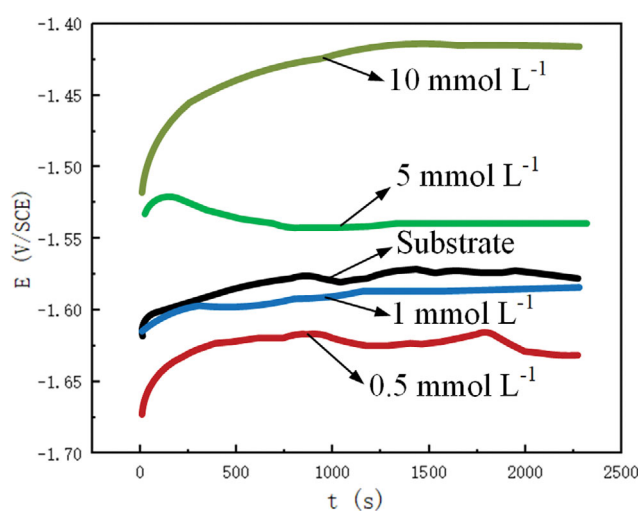
Fig. 9. Open circuit potential of samples in corrosive solution with different sodium silicate concentrations [86].

9. At this time, the protection film is formed rapidly and stably, and the density is improved [86,92]. However, a high concentration does not necessarily mean an enhanced effect. Excessively concentrated silicate will over-polymerize and fail to form a silicate protective film. In an aerated soft water medium, the corrosion inhibition efficiency of 30 ppm sodium silicate is only 54.76% [93]. The recent applications of sodium silicate in different corrosive medium are summarized in Table 4.

However, single silicate corrosion inhibitors slowly form an in-

Table 4. Applications of sodium silicate corrosion inhibitor

Reference	Corrosive medium(Solution)	Protected objects	Optimum content	Corrosion inhibition rate
Gao [86]	148 mg/L Na_2SO_4+138 mg/L $NaHCO_3$+165 mg/L NaCl (PH=8.2)	Magnesium material	1,220 mg/L	99%
Sarah kareem [87]	3% NaCl (PH≈7)	Carbon steel	2%	92.5%
Ming [94]	Water-based cutting fluid	Aluminum material	0.8%	89.11%
Li [95]	H_2O	Aluminum material	$300×10^3$ mg/L	95%
Li [96]	H_2O	45 steel	$10×10^3$ mg/L	60%
Mainier [97]	3.5% NaCl (PH≈7)	Carbon steel	1,250 mg/L	92%
Salami [98]	1 M NaOH+30 g/L $Na_2B_4O_7$ (PH=14)	Magnesium material	$30×10^3$ mg/L	98.7%
Zheng [92]	0.01 M NaOH (PH=12)	Aluminum material	1,220 mg/L	97.23%
Ma [99]	0.6 M NaCl (PH≈7)	Magnesium alloy	4,880 mg/L	97.7%

hibitor film that is uneven, porous and has poor water resistance. Corrosive substances easily penetrate the film pores to corrode metals and form silica scales; hence, silicate corrosion inhibitors are generally used in conjunction with organic corrosion inhibitors [100].

4. Other Inorganic Corrosion Inhibitors

In addition to the above-mentioned molybdate, tungstate and silicate corrosion inhibitors can replace environmentally unfriendly corrosion inhibitors such as nitrates and chromate. Many new types of inorganic salt corrosion inhibitors have been recently developed.

Given the similar properties of group IV elements and group VIB elements, the inorganic salt corrosion inhibitors of zirconium [101], titanium [102,103], and hafnium [103] in group IV elements have been widely explored. Zirconium, titanium, and hafnium elements have high reactivity and a strong affinity with oxygen. These materials are called oxidation corrosion inhibitors. As long as a small amount of oxygen or water is present in the environmental medium, a continuous, stable, and strong oxide film can be formed, and the damaged film can be automatically repaired. Vanadium salts [104], tin salts [105], and rare earth elements [106] also have excellent corrosion inhibition properties. At present, the research and application of new inorganic corrosion inhibitors in cutting fluids is relatively lagging behind, and many issues remain controversial. The current problems of inorganic corrosion inhibitors are mainly high cost, long molding time, complex application process, and long processing time.

5. Summary

At present, inorganic corrosion inhibitors mainly have disadvantages such as large dosage, environmentally damaging, and expensive. The compound use of inorganic and organic corrosion inhibitors can ameliorate the above shortcomings. Inorganic corrosion inhibitors are generally used as auxiliary additives, and organic corrosion inhibitors are generally used as the main material [80]. Compared with inorganic corrosion inhibitors, organic corrosion inhibitors are widely used because of their low cost, environmental protection, and wide application range [107]. Moreover, they form an adsorption film on a material's surface through electrostatic force or chemical bonding. Compared with oxide or precipitation film, the adsorption film does not fall off and has good protective effect on metals [108].

ORGANIC CORROSION INHIBITORS

Organic corrosion inhibitors are usually composed of two parts: one is the polar group containing lone electron pairs and electronegative elements such as O, N, S, and P and a double bond or triple bond containing π electron. The other part is a non-polar group (hydrophobic chain) composed of C and H atoms [25].

First, the corrosion inhibitor is dissolved in the solvent, and the polar groups and π bonds are adsorbed on the metal substrate by reacting with the blank d orbital of the metal, thereby changing the electric double layer structure on the metal surface and im-
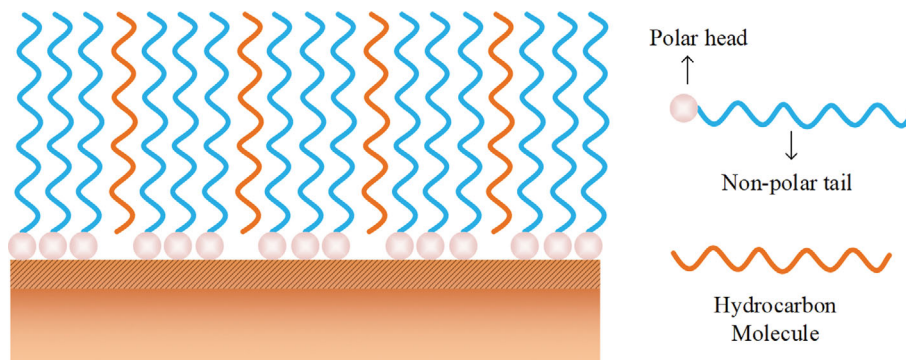
Fig. 10. Film formation mechanism of organic corrosion inhibitor [33].
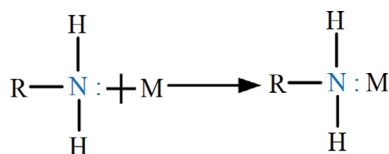
Fig. 11. Chemisorption process.

Fig. 12. Adhesion energy between inhibitor and passivation film [118].

proving the activation energy of substrate corrosion reaction. The non-polar chains are oriented in the medium to form a hydrophobic film (Fig. 10), which effectively isolates the contact between the metal and the corrosive medium, hinders the diffusion of corrosion reaction products, and reduces the corrosion rate [34].

The non-polar tail of the corrosion inhibitor molecule can physically adsorb the hydrocarbon molecules in the base oil and thereby increase the thickness and effectiveness of the hydrophobic corrosion barrier [33] as shown in Fig. 10.

The adsorption of polar groups can be physical adsorption, chemical adsorption, or both.

The central atom of polar groups (such as N, S, and P) contains a lone pair of electrons that easily combine with hydrogen protons to form cations. The van der Waals force between the cation and the metal makes the organic corrosion inhibitor adsorb on the metal surface, a process called physical adsorption. This phenomenon is reversible, prone to desorption, and less affected by temperature. No specific combination occurs between metal and corrosion inhibitor, and the process only changes the charge state of the metal surface [109].

Compared with physical adsorption, chemical adsorption is stronger, more stable, and plays the main role of adsorption. The corrosion inhibitor molecules or ions form coordination bonds with the metal surface [76]. The schematic of chemical adsorption function is shown in Fig. 11.

In cutting fluid field, common organic corrosion inhibitors include alcohol amines, carboxylic acids, amides, carboxylic acid salts, nitrogen heterocyclic compounds, phosphate esters, and borate esters.

1. Alkanolamine

Common alkanolamine corrosion inhibitors include monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), triethanolamine (TEA), diethylene glycol amine (DGA), and 2-amino-2-methylpropanol (AMP-95). Monoethanolamine is highly toxic, and 26 countries/regions have established a limit value for this substance. Other alcoholamine corrosion inhibitors also have toxicity but at relatively low levels [110].

Alcoholamine corrosion inhibitors form coordination bonds with the metal surface through nucleophilic active sites such as nitrogen and oxygen in the molecule, and the carbon atoms in the molecule can accept the feedback bond formed by the electrons given by the metal surface [111]. During the formation of the corrosion inhibitor film, the structure of the electric double layer changes, the activation energy of the metal ionization process is improved, and the corrosion of the metal by the corrosion ion is reduced [112].

Liu et al. [113] found that adding MEA or TEA in the grinding fluid can inhibit the corrosion of cast iron. Although the addition of MEA to the cutting fluid has a certain anti-rust effect on
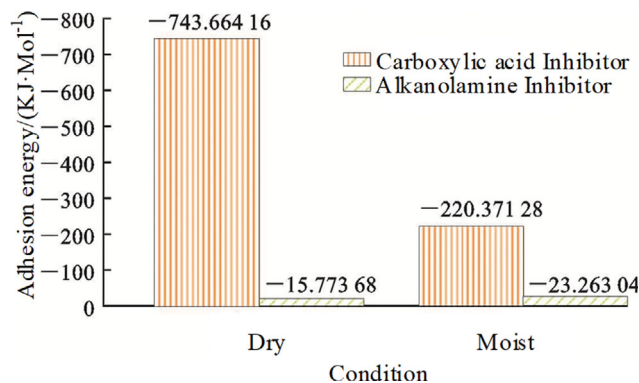
cast iron, this method has not yet reached the standard and requires the addition of carboxylic acid corrosion inhibitors [114].

In cutting fluids, alcoholamine corrosion inhibitors fail to inhibit, and even accelerate, the corrosion of certain metals and cutting tools. Chen [91], Xu [115], and Liang [116] found that several organic alcohol amine corrosion inhibitors (MEA, DEA, TEA, DGA, and AMP-95 widely used in cutting fluid) can protect cast iron and grinding wheel but have a corrosive effect on copper and aluminum. Under alkaline conditions, copper and alcohol amines combine to form various complexes and dissolve in the processing liquid. Alcohol amines have a certain corrosive effect on tungsten carbide tools, thus allowing TEA to form a stable complex with cobalt and dissolve in the processing liquid [117].

Compared with carboxylic acid, alcoholamine molecules are less polar and have relatively poor interaction with the matrix. As shown in Fig. 12, alcohol amine molecules have weaker corrosion inhibition effect than carboxylic acid molecules [118].

2. Carboxylic Acid

Carboxylic acid is a compound containing carboxyl functional group (-COOH) and has a general chemical formula of R-COOH (Fig. 13). Depending on the number of carboxyl groups, these materials are classified into monoacid, diprotic acid, and polybasic acid. Carboxylic acids and their derivatives contain polar groups such as -COOH, which have certain affinity with metals and easily adsorb on the metal surface. The hydrophobic hydroxyl group forms a protective film on the metal surface that can lubricate or prevent rust [119].

Different types of carboxylic acid inhibitors are often combined to improve the inhibition effect. The inhibition effect of the same type of acid has minimal difference with regard to molecular weight, and the improvement of inhibition performance of the same type of acid with different molecular structures is minimal [120].
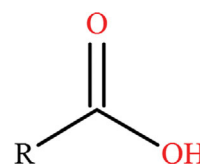

Fig. 13. Chemical structure of carboxylic acid.

The inhibition performance of carboxylic acid type corrosion inhibitor is closely related to its concentration, number of carbon atoms of hydrocarbon group, number of carboxylic group, and pH value.
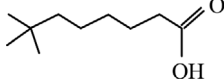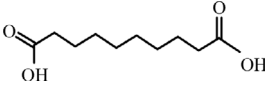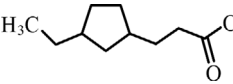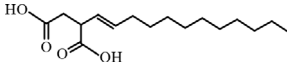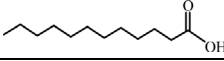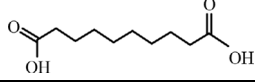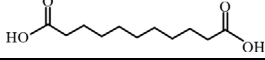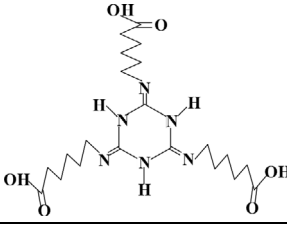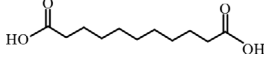
With the increase in the concentration of carboxylic acid inhibitor, the corrosion inhibition film becomes compact and the inhibition effect improves [121]. However, most corrosion inhibitors are electrolytes, prone to electrolysis, and influence other cutting fluid properties, such as emulsion stability and lubrication performance. Hence, the dosage shoul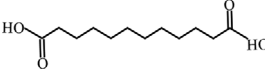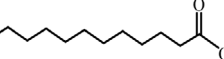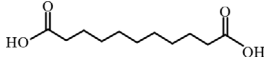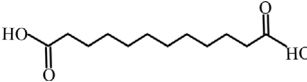d not be excessively large [122]. In general, the amount of single inhibitor used in cutting fluid is generally less than 4%, and the content of inhibitor which has great influence on the performance of diluent in cutting fluid should be less than 2% [120].

In a certain range, the inhibition effect is good when the alkyl carbon chain is long. The length of normal alkyl group is generally between 10 and 12 carbon atoms. However, excessive carbon is liable to cause foam problems and reduce water solubility; hence, the number does not usually exceed 12 carbon atoms [123].

Within a certain range, the inhibition effect is good when the number of polar groups of organic acid inhibitor molecules is high. The polarity of a single carboxyl group is not sufficiently strong; a

Table 5. Application of carboxylic acid corrosion inhibitor in cutting fluid concentrate

Reference	Corrosion inhibitor	Chemical structure	Optimum content	Protected objects
Liu [120]	Neodecanoic acid		3.75%	Cast iron
	Sebacic acid		3.75	
	Tall oil fatty acid		3%	
Li [125]	Dodecenyl succinic acid		10%	Aluminum material
Snyder [126]	Lauric acid		1.2%	Cast iron
	Sebacic acid		0. 5%	
	Undecanedioic acid		0.38%	
	6,6′,6″-(1,3,5-triazine-2,4,6-triyltriimino) trihexanoic acid		2%	
Kirsch [127]	Undecanedioic acid		5-10%	Cast iron
	Dodecandioic acid			
Lei [128]	Lauric acid		3-8%	Cast iron
	Undecanedioic acid			
	Dodecandioic acid			

polycarboxylic acid molecule has multiple polar groups adsorb on the metal surface, thus forming a dense protective film [123]. However, if the molecule has excessive polar groups, then its volume becomes large. Owing to the steric hindrance effect, the adsorption energy of the molecule will be reduced and the inhibition effect will be affected [121].

Within a certain range, the increase in pH value increases the inhibition effect of carboxylic acid, completely dissolves the organic acids, and firmly adsorbs the corrosion inhibitors on the metal surface [123].

Some carboxylic acid type corrosion inhibitors (such as dicarboxylic acid) tend to precipitate in the presence of Ca^{2+} or Mg^{2+}, thus leading to the lack of corrosion inhibition performance [124]. Therefore, the hardness of water should be strictly controlled when using carboxylic acid corrosion inhibitors. The application of carboxylic acid corrosion inhibitor in cutting fluid concentrate is shown in Table 5.

In cutting fluid, most organic carboxylic acids, such as undecanedioic acid, L190 terpolycarboxylic acid, and sebacic acid, can only inhibit the corrosion of aluminum alloys up to grade C, but have good corrosion inhibition performance for cast iron. However, some carboxylic acid corrosion inhibitors (such as dodecenylsuccinic acid) have poor corrosion inhibition effect on cast iron, but the corrosion inhibition efficiency on aluminum can reach more than 90% [125].

At present, most carboxylic acid inhibitors are used in combination to achieve corrosion inhibition. The commonly used carboxylic acid inhibitors in cutting fluid include neodecanoic acid, sebacic acid, dodecenylsuccinic acid, lauric acid, undecane undecanedioic acid, and decanedicarboxylic acid. Dodecenyl succinic acid is a corrosion inhibitor with good corrosion inhibition effect on aluminum alloy and poor corrosion inhibition effect on cast iron. In addition, most carboxylic acid inhibitors have excellent corrosion inhibition effect on cast iron but poor corrosion inhibition effect on aluminum.

3. Amide

Organic acids are easily soluble in ethanol at room temperature but hardly soluble in water. Some common carboxylic acid corrosion inhibitors such as sebacic acid [129], oleic acid, and dodecenyl succinic acid [130] have limited application in water-based cutting fluids due to their poor water solubility and hydrolytic stability. In traditional processing, alcoholamine corrosion inhibitors are often used in combination with nitrite to enhance corrosion inhibition effect [131]; however, nitrite can react with organic amines to form carcinogen nitrosamine, which is not in agreement with the concept of green machining. Amide and carboxylic acid salts formed by the reaction of alcohol amines and carboxylic acids can effectively solve the above problems.

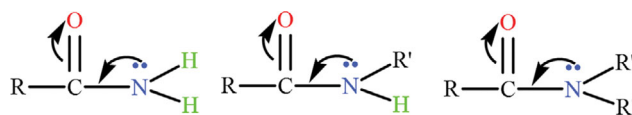The reaction of alcohol amines and carboxylic acids can intro-

Fig. 14. Chemical structure of amide.

duce hydrophilic groups into the carboxylic acid molecules. Compared with carboxylic acid and alcohol amine, the lubricity, corrosion inhibition [130], and water solubility [132] are improved. In addition, this method is green and has low toxicity.

As nitrogen-containing carboxylic acid derivative, the structure of amide is shown in Fig. 14. The amide molecule can contain carboxylic acid and alcohol amine molecule corrosion inhibition groups, and its performance is better than that of single alcohol amine and carboxylic acid molecule of the same group.

When working, the lone pair electrons of the polar group in the amide molecule form a stable coordination bond with the empty orbital of the iron atom on the metal surface to cause adsorption, and the non-polar long hydrocarbon chain deviates from the metal surface and self-assembles into a close-packed hydrophobic film at a certain inclination angle to inhibit corrosion [133].

Several scholars have studied the application in water-based cutting fluids. Gan et al. [129] found that dodecenylsuccinic acid diethanolamide corrosion inhibitor can adsorb the iron atoms on the metal surface through the nitrogen atoms and carboxyl oxygen atoms in the molecules, thus preventing other molecules such as oxygen and water from contacting with the metal surface and inhibiting rust. These materials can be used as the inhibitor of semi synthetic cutting fluid. Zhang et al. [134] found that alkanolamide molecules contain a large number of hydrocarbon groups, amide groups, and other hydrophobic groups; have strong adsorption power to metals; and easily adhere to the metal surface to form a hydrophobic protective film. In synthetic water-based cutting fluid, this material can produce good corrosion inhibition effects on cast iron, aluminum, and copper.

For water-based cutting fluids, extreme pressure performance is also a necessary condition for application. Zhao et al. [135] studied the friction mechanism of amines and amide compounds and found that amines mainly rely on hydroxyl to adsorb on the friction surface. In addition to relying on hydroxyl adsorption, amide compounds also generate C-N groups to adsorb on the friction surface, thus providing them with excellent lubricating properties. Khalkaret et al. [136] prepared fatty acid amides with good extreme pressure and anti-wear performance as shown in Fig. 15. The application of amide corrosion inhibitor in cutting fluid concentrate is shown in Table 6.

In cutting fluid, amide corrosion inhibitors are mainly used for the protection of cast iron. However, in aqueous solution, the solu-
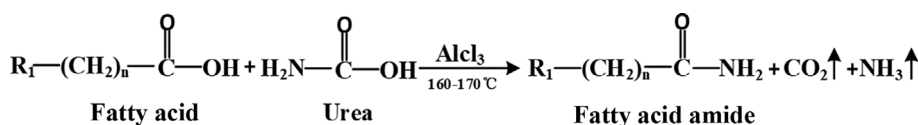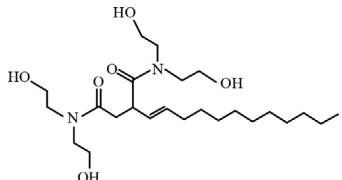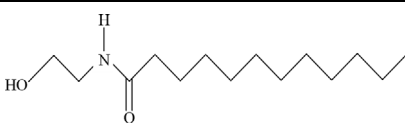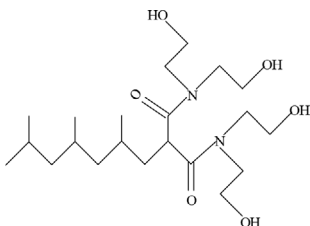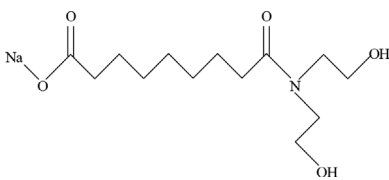

Fig. 15. Preparation of fatty acid amides [136].

Table 6. Application of amide corrosion inhibitor in cutting fluid concentrate

Reference	Corrosion inhibitor	Chemical structure	Protected objects	Optimum content
Gan [129]	Dodecenylsuccinic acid diethanolamide		Cast iron	15%
Zhang [134]	Alkanolamide		Cast iron, Copper material	13%
Li [137]	Coconut oil monoethanolamide		Cast iron	17%
Ding [138]	Dodecenyl succinic acid diethanolamide		Cast iron	8-16%
Liu [139]	Sodium azelaic acid amide		Cast iron	2-8%

bility of amide compounds in water and amide polarity bond is smaller than carboxylic acid salt. Under the same carboxylic acid group, the inhibition effect of amide is weaker than that of carboxylic acid salt [140].

4. Carboxylic Acid Salt

The corrosion inhibition principle of carboxylic acid salt is in line with the general principle of organic corrosion inhibitors, that is, the polar groups in the molecule have a certain affinity with the metal and are easily adsorbed on the metal surface. The hydrophobic hydroxyl non-polar chains are aligned in the medium to form a hydrophobic film that effectively isolates the contact between the metal and corrosive medium.

Li et al. [114] found that in cutting fluids, the highest corrosion inhibition effect of dicarboxylic acid (C12M1)+tricarboxylic acid (L190plus) on cast iron has up to grade B. When triethanolamine and methyldiethanolamine are added, a carboxylic acid salt corrosion inhibitor is formed and the effect for can reach grade A, in line with international standards.

In the cutting fluid, the triethanolamine oleate can be adsorbed on the tool surface to separate the cemented carbide surface from the external medium; the combined action of the polar and non-polar groups prevents the leaching of elements on the cemented carbide blade surface [116,117].

For carboxylic acid salt, the inhibition performance increases with the hydrocarbon group carbon chain length in molecule. However, if the carbon chain is excessively long, then the water solubility and the effective concentration in water will decrease, and the corrosion inhibition effect will be affected. Under the same chain length, a large number of polar groups in the molecule leads to a strong polarity and improved corrosion inhibition performance. Therefore, the corrosion inhibition performance of the dibasic acid alcohol amine salt is better than that of monobasic acid alcohol amine salt with the same carboxylic acid carbon chain length [141]. The application of carboxylic acid salt corrosion inhibitor in cutting fluid concentrate is shown in Table 7.

In cutting fluids, sebacic acid triethanol has poor corrosion inhibition effects on aluminum alloys and magnesium alloys. A low concentration of triethanolamine oleic acid can protect aluminum alloy and magnesium alloy, but the corrosion inhibition effect gradually decreases when the dosage increases. Meanwhile, triethanolamine oleate does not have a good corrosion inhibition effect on cast iron mainly due to inadequate surface tension of the solution, weak intermolecular force of the molecules, and loose adsorption film formed on the surface of the test piece [125].

In cutting fluids, triethanolamine oleate has good inhibition effects on carbide tools, aluminum, and magnesium alloys. Special attention should be paid to its usage. Sebacic acid triethanol has good corrosion inhibition effect on cast iron but poor corrosion

Table 7. Application of carboxylic acid salt corrosion inhibitor in cutting fluid concentrate

Reference	Corrosion inhibitor	Chemical structure	Protected objects	Optimum content
Liang [116]	Triethanolamine oleate		Carbide tools	16-20%
Li [125]	Triethanolamine oleate		Aluminum material	10%
			Magnesium material	10%
Liu [139]	N-octanoic acid monoethanolamine		Cast iron	2-8%
Hao [142]	Sebacic acid triethanolamine		Cast iron Steel	5%
Sun [143]	Azelaic acid triethanolamine		Cast iron, Aluminum material	10%
Zhang [144]	Triethanolamine oleate		Carbide tools	12%
Fu [145]	Triethanolamine oleate		Aluminum material	14%
Chen [146]	Triethanolamine nitrobenzoate		Carbide tools	20%

inhibition effect on aluminum. Most carboxylic acid salts have good corrosion inhibition effects on cast iron. Among them, azelaic acid triethanolamine shows excellent corrosion inhibition performance on aluminum and cast iron [122,142].

5. Nitrogen Heterocyclic Compounds

Many nitrogen heterocyclic compounds, such as thiadiazoles and triazoles, can be effective ash-less metal corrosion inhibitors [147].

5-1. Thiadiazole

Thiadiazole is a five-membered ring compound containing S and N heteroatoms (Fig. 16(a)). The compound monomer itself does not exist. The main existence form is a derivative in which the hydrogen atoms at positions 2 and 5 are substituted (Fig. 16(b)). 2,5-Di-x-1,3,4-thiadiazole has a wide range of applications in field of corrosion inhibition and friction [148]. Among which, X is mainly mercapto and alkyl.

Thiadiazole has excellent corrosion inhibition performance to
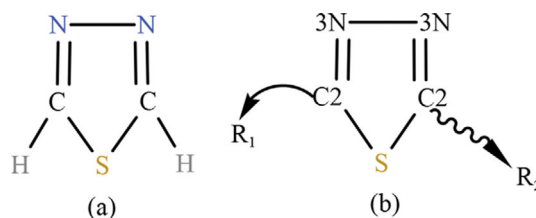
Fig. 16. Structure diagram of thiadiazole corrosion inhibitor [148] ((a) thiadiazole monomer, (b) Structure of thiadiazole corrosion inhibitor).

copper. The N, S, and other polar groups in the molecule bind to the metal surface atoms in the form of coordination bonds to cause adsorption, and the hydrophobic group R_2 generates an inhibitor film on the metal surface and hinders the migration of corrosive
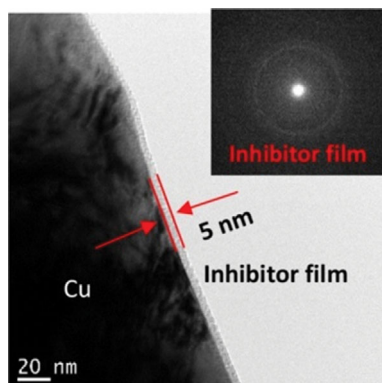
Fig. 17. Thiadiazole inhibitor film [149].

medium to metal interface as shown in Fig. 17. The hydrophilic group R_1 can improve the solubility in water to increase corrosion inhibition performance [149].

With 2,5-dimercapto-1,3,4-thiadiazole (DMTD) as an example, the DMTD molecule reacts with the metal copper through the two thiol groups outside the ring to form the monosulfide of DMTD salt, is then coordinated with Cu ion through the two sulfur atoms outside its ring, and finally is connected by Cu ion to form a solid 1D chain polymer film that is adsorbed on the copper surface (Fig. 18) [150].

To a certain extent, a long alkyl chain of the thiadiazole corrosion inhibitor leads to a good corrosion inhibition effect [151]. However, the chain length of the alkyl chain is inversely proportional to the solubility. The solubility of molecules decreases when the chain length is excessively long. Therefore, the chain length should be determined according to the principle of Similar Solubility Parameters. In addition, a long alkyl chain leads to a great solvation energy and good adsorption capacity of the molecule in the solvent medium. In summary, the corrosion inhibition efficiency of thiadiazole molecules is related to the alkyl chain length and depends on the solubility of the corrosion inhibitor molecules and the solvation energy due to the introduction of solvent water [152].

Based on the steric hindrance effect, Liu et al. [153] found compared with the aryl group, the corrosion inhibition performance is better when the non-polar group is alkyl due to the larger volume of the aryl group and more serious resistance in the adsorption process.

The corrosion inhibition performance of thiadiazole is better than that of other types of copper corrosion inhibitors [154]. Xiong

Fig. 19. Structure of triazole compounds.

Fig. 20. Structure of benzotriazole.
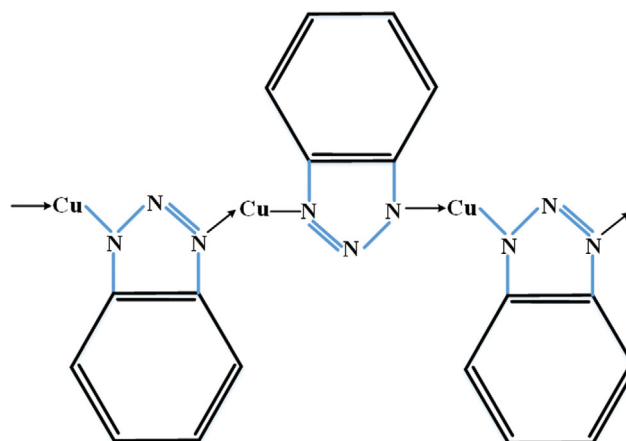
Fig. 21. Mechanism of benzotriazole on Cu [158].

[149], Li [155], and Scherer et al. [156] studied its performance in cutting fluid. However, this material is expensive and toxic. Compared with thiadiazole, low-priced triazole compounds are currently the main research and application targets of copper corrosion inhibitors in cutting fluids.

5-2. Triazole
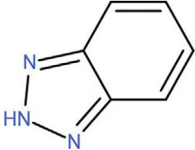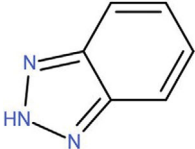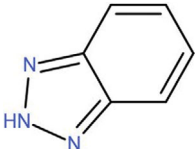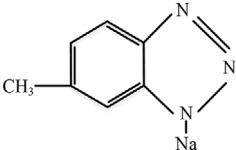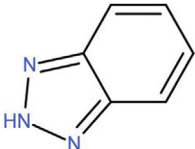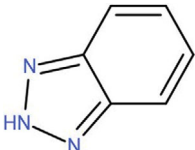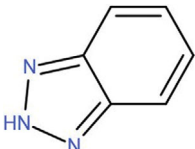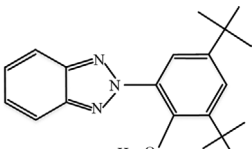
The structure of triazole compounds is shown in Fig. 19. Their

Fig. 18. Mechanism of DMTD on Cu [150].

toxicity is lower than that of other nitrogen heterocyclic corrosion inhibitors. The triazole corrosion inhibitors in cutting fluid mainly include triazole derivatives and benzotriazole inhibitors Fig. 20 [157].

Benzotriazole is an excellent copper metal corrosion inhibitor. The copper atom replaces the hydrogen atom next to the NH func-

Table 8. Application of triazole corrosion inhibitor in cutting fluid concentrate

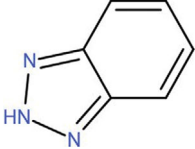| Reference	Corrosion inhibitor	Chemical structure	Protected objects	Optimum content
Liu [113]	Benzotriazole		Cast iron	0.3%
Liang [116]	Benzotriazole		Carbide tool	1%
Liu [120]	Benzotriazole		Copper material	>0.2%
Zhang [123]	Benzotriazole		Copper material	0.1%
Kirsch [127]	Methyl-benzotriazole sodium salt		Copper material	0.4%
Zhang [144]	Benzotriazole		Carbide tool	0.6%
Liang [161]	Benzotriazole		Cast iron, Copper material	0.2%
Wei [162]	Benzotriazole		Copper material	0.1-0.2%
Singh [163]	Di-tert-butylated benzotriazole		Cast iron, Copper material	0.035%

tional group in a benzotriazole molecule via the covalent bond and connects with another benzotriazole. The free electron pairs on the triazole molecule connect in the form of coordination bonds to form semi-permanent polymer complexes that exhibit corrosion inhibition effect as shown in Fig. 21 [158].

Chen [91] studied the corrosion inhibition effects of benzotriazole (BTA), sodium silicate, and triethanolamine on copper in sodium chloride solution and found that at inadequate concentration, sodium silicate and triethanolamine will accelerate the corrosion of copper. Only BTA has no side effects. Kumari et al. [159] found that in alkaline medium, the maximum corrosion inhibition rate of 4-amino-5-(4-nitrophenyl)-4H-1,2,4-triazole-3-thiol to aluminum alloy can reach 72.3%, and the efficiency decreases with the increase in temperature. The 2-aminobenzothiazole and benzotriazole compound system has a synergistic effect for protecting Cu; however, when the concentration is excessively high, the corrosion inhibitor molecules will agglomerate and decrease the corrosion inhibition efficiency [160].

In cutting fluids, triazole corrosion inhibitors can also protect carbide tools. The protection mechanism is as follows: the lone pair of electrons in triazole can cooperate with the metal to form insoluble complexes. The complexes are adsorbed on the surface of the cemented carbide tool and then polymerize to form a layer of precipitation film, which protects the cutting tool [116,117]. The application of triazole corrosion inhibitor in cutting fluid concentrate is shown in Table 8.

Zhang et al. [123] found that the corrosion inhibition performance of benzotriazole for copper is better than that for aluminum. In addition, under certain circumstances, benzotriazole in cutting fluids does not have a good corrosion inhibition effect on aluminum alloys [164]. Fan et al. [165] found that the inhibition effect of benzotriazole on cast iron is not outstanding.

In summary, triazole corrosion inhibitor has the highest corrosion inhibition reliability for copper, followed by benzotriazole that can also play a good protective effect on carbide tools.

6. Phosphate Ester

Phosphate esters are a class of compounds formed by the substitution of hydrogen in the phosphoric acid group. Their structure is shown in Fig. 22 [166]. Compared with inorganic phosphorous salt, organic phosphate ester have lower phosphorus content, are not easily hydrolyzed into orthophosphate, and have certain toxicity to the human body [167].

Compared with silicate and other types of water-based cutting fluid additives, phosphate ester compound has outstanding corrosion inhibition effect on aluminum alloy [162] and can be adsorbed on the alumina layer on the surface of aluminum alloy through
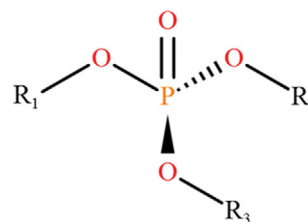

Fig. 22. Structure diagram of organic phosphate ester [166].

hydrogen bonds and then condensed with alumina. Finally, a resonance-stable protective film is formed, and the mechanism is shown in Fig. 23. Water hardness seriously affects the corrosion inhibition performance of inhibitors and thus must be controlled in industrial production. The anti-rust effect can be improved with the gradual increase in the pH value of the diluent [164].

Li [89] and Zhang et al. [168] believed that the corrosion inhibition ability of phosphorus-containing additives is related to the following factors: the stability of polar groups (the weaker the stability, the easier it is to adsorb metals), the chain length of the hydrophilic group (the longer the chain, the stronger the hydrophilicity of the molecule, which is not conducive to the formation of an adsorption film with good shielding ability on metal surface), and the type of adsorption film formed by the corrosion inhibitor and the metal surface (the corrosion inhibition ability of chemical adsorption is better than physical adsorption). The application of phosphate ester corrosion inhibitor in cutting fluid concentrate is shown in Table 9.

Although some phosphate ester corrosion inhibitors have excellent corrosion inhibition performance for aluminum material, their use is limited due to their poor compatibility with mother liquor [89]. Phosphorus-containing additives can prevent rust from cast iron and other ferrous metals only in large doses [164]. In addition, grinding fluids containing phosphate esters even will corrode cast iron [172].

In summary, phosphate ester compounds are the main corrosion inhibitors for aluminum material in cutting fluids. Special attention should be paid to their poor corrosion inhibition effects on ferrous metals such as cast iron. These compounds can sometimes cause corrosion and hence cannot be used as a universal corrosion inhibitor.

7. Overview of New Green Non-toxic Corrosion Inhibitors

With the increasing demand for innovation in mechanical components and manufacturing fields, the quantity of machining operations has increased sharply. Metalworking fluids are one of the most important effluents that are processed into the environment
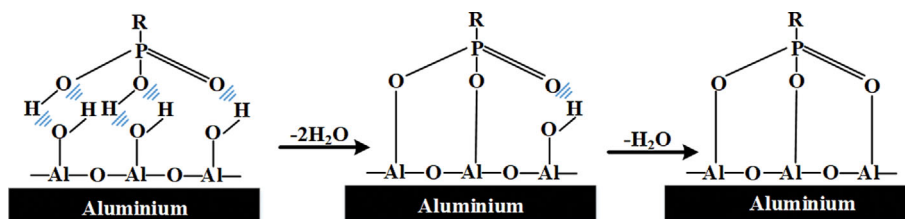

Fig. 23. Corrosion inhibition mechanism of phosphate ester [164].

Table 9. Application of phosphate ester corrosion inhibitor in cutting fluid concentrate
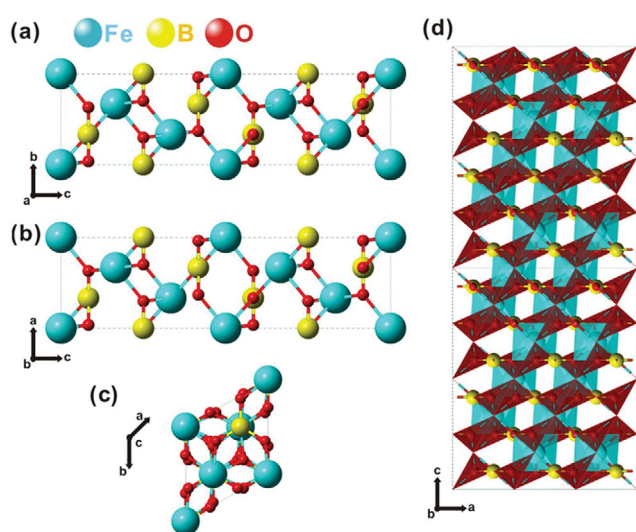
Reference	Corrosion inhibitor	Chemical structure	Protected objects	Optimum content
Li [89]	ASI-80 (Hydroxyl phosphonate ester derivatives)		Aluminum material	2.5%
Zhang [164]	Alkyl polyoxyethylene ether phosphate		Aluminum material	2%
Li [169]	Nonylphenol polyoxyethylene ether phosphate ester		Aluminum material	2-3%
He [170]	Acid phosphate ester		Aluminum material	2-3%
Liu [171]	Fatty alcohol polyoxyethylene ether phosphate ester		Aluminum material, Magnesium material	1.5%

during metal processing [173]. The estimated global annual waste of cutting oil exceeds 20 billion liters [174].

Traditional organic corrosion inhibitors have low toxicity, but their annual emissions are tremendous [175,176]; therefore, the impact on the environment is relatively large. The low toxicity of organic corrosion inhibitors prevents their application in the medical or food fields. Therefore, new, green non-toxic corrosion inhibitors have been explored.

7-1. Borate Ester

Organic borate ester compounds are a novel, non-toxic, and odor-less additive with good corrosion inhibition, anti-wear, and anti-bacterial properties [177]. Boron-containing corrosion inhibitors have a wide range of raw materials, low price, and excellent molecular design [178].

The basic structures of boron type corrosion inhibitor are $[BO_3]^{3-}$ triangle planar and $[BO_4]^{4-}$ tetrahedron. These B-O anions are connected by the same atom or edge to form different complicated polyanion clusters [179,180], and these B-O anions and polyanion clusters can combine with metal ions, including Al and Fe, to form metal-O-B inhibitor film [181,182] as shown in Fig. 24.

However, the boron atom in borate ester compound molecule is SP2 hybridized, and an empty P orbital is also present. Nucleophile elements (such as water) can easily attack this empty P orbital, leading to hydrolysis [183] as shown in Fig. 25.

The hydrolytic stability of borate esters can be improved in two ways: coordination method, and change the structure of borate ester.

(1) Coordination method

Coordination is to introduce nitrogen or other electron-rich

Fig. 24. Configuration of the FeBO$_3$ structure from (a) a axis, (b) b axis, and (c) c axis. (d) extended structure of FeBO$_3$ from b axis [182].
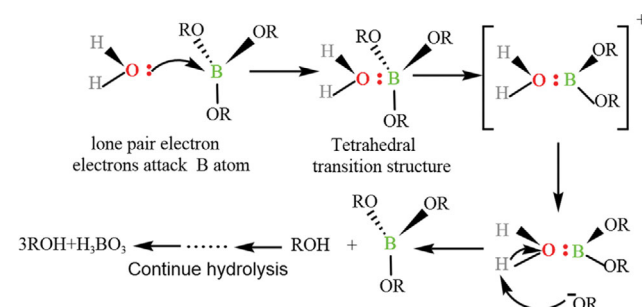
Fig. 25. Hydrolysis of borate ester [184].

Fig. 26. Preparation of PBDTC [187].

Fig. 27. Outline of the synthesis of DBDB and OMDB [184].

(1) Esterification Reaction:
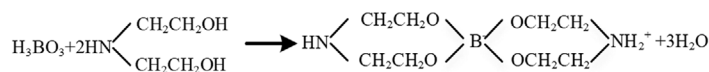
(2) Acylation Reaction:
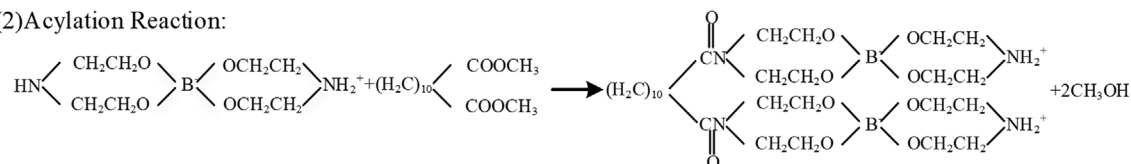
Fig. 28. DBE (1) and DAB (2) synthesis route and principle [131].

atoms into the molecule to ensure that the lone pair of electrons occupy the empty orbital of the boron atom to form an internal coordination bond, thereby increasing the steric hindrance of the molecule. As a result, water molecules cannot to attack the boron atom empty orbital, and the hydrolytic stability of the borate ester is improved [185]. The introduction of nitrogen atoms with a lone pair of electrons into the borate ester molecule is regular practice in current research [186].

(2) Changing structure method

Changing structure method is to increase the steric hindrance of the molecule to ensure that the steric orbital of the boron atom cannot be attacked by water molecules. One technique is to introduce alcohol amine structure, long-chain alkyl structure, and nitrogen heterocyclic structure to the molecule.

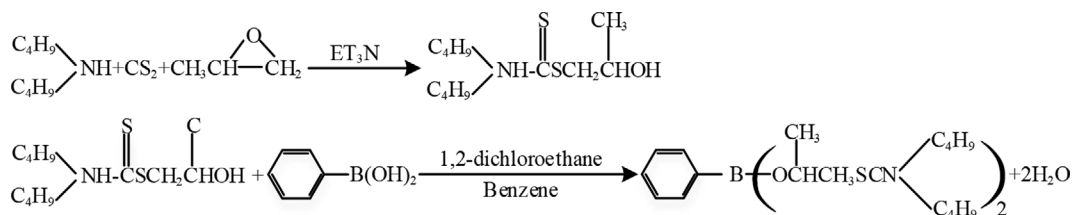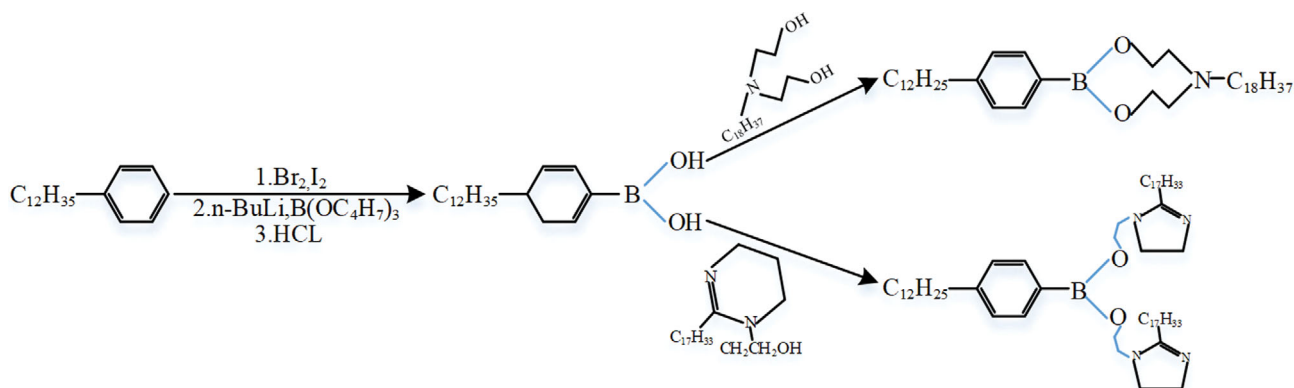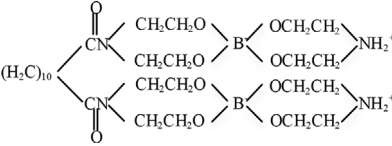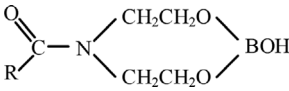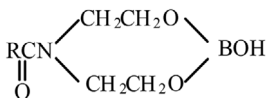Based on the theory of Stable Benzylic Cation, Wang et al. [187] introduced a benzene ring into the borate eater molecule to synthesize a borate ester additive (PBDTC) with high hydrolytic stability. This process further improved the hydrolysis stability of borate ester, and the preparation process is shown in Fig. 26.

Following up on this research, Li et al. [184] directly linked long-chain alkyl phenyl with electron deficient boron to prepare two novel nitrogen-containing long-chain phenylborate esters with excellent hydrolytic stability: DBDB (2-(4-dodecylphenyl)-6-octadecyl-1,3,6,2-dioxazaborate) and OMDB (dbis(2-(2-((E)-heptadec-8-enyl)-4,5-dihydro-1H-imidazol1-yl) ethyl)-4-dodecylphenylborate) (Fig. 27).

Zhou [131] synthesized dodecanedioic acid diamide diethanolamine borate ester (DAB) through diethanolamin borate ester (DBE). The synthesis route and principle are shown in Fig. 28. Compared with DBE, DAB has a better anti-rust effect, more polar groups in the molecule, thicker film adsorbed on the metal surface, and better anti-rust ability.

pH value has a more serious influence on the hydrolysis rate of borate esters than the molecular structure. Compounding borate esters and amines can adjust the pH value to improve the hydrolysis stability and the oxidation resistance of the cutting fluid, thereby protecting the metal [188]. The application of borate ester corrosion inhibitor in cutting fluid concentrate is shown in Table 10.

Table 10. Application of borate ester corrosion inhibitor in cutting fluid concentrate

Reference	Corrosion inhibitor	Chemical structure	Protected objects	Optimum content
Zhou [131]	Dodecanedioic acid diamide diethanolamine borate ester		Steel, Cast iron	50%
Fu [145]	Triethanolamine borate ester		Aluminum material	1.2%
Wang [186]	Triethanolamine borate ester		Steel, Cast iron	0.5-2.5%
Li [189]	Triethanolamine borate ester		Cast iron	3%-10%
Liu [190]	Oleic diethanolamide borate ester		Cast iron	14%
Yuan [191]	Twelve acid diethanolamide boric acid ester		Cast iron, Aluminum material, Copper material	11.3%

Compared with other corrosion inhibitors, borate esters have a particularly outstanding effect on steel corrosion. Modifying borate ester molecules through molecular design theory can provide it with good corrosion inhibition effects on steel, cast iron, copper material, and aluminum material. This compound can be a general corrosion inhibitor that is green, non-toxic, and environmentally friendly.

7-2. Natural Plant Extracts

Corrosion inhibitors can also be extracted from natural plant organs. The corrosion inhibition mechanism of these inhibitors is mainly adsorption type. Owing to their green, non-toxic, easy to degrade, and other environmentally friendly characteristics, these materials have been a popular research object.

In plant extracts, the aromatic ring or heteroatom (S, N, O, and P) polar adsorption center in the molecule plays the role of corrosion inhibition. These polar adsorption centers can be adsorbed on the metal substrate to form a protective film, thereby effectively inhibiting metal corrosion [192]. In alkaline environment, plant extract corrosion inhibitors have good corrosion inhibition effects on metals such as steel [193], copper [194], and aluminum [195]; however, this phenomenon does not necessarily mean that they can be directly applied to cutting fluids. The application in cutting fluids does not only focus on the corrosion inhibition performance but also the combination effect with the base fluid.

Plant extracts contain various phytochemical components, but only a few specific components can protect metals [196]. Therefore, the individual active ingredients must be separated and evaluated through high performance liquid chromatography-mass spec-

trometry or gas chromatography-mass spectrometry.

In addition, the conventional extraction process has problems such as long processing time and difficult control of the processing temperature [197,198]. In the future, developing new extraction technologies is also a key direction in natural plant extract corrosion inhibitor.

8. Influence of Molecular Structure and Temperature on Corrosion Inhibition Performance

8-1. Molecular Structure of Corrosion Inhibitor

(1) Polar group

The influence of polar groups on the corrosion inhibition molecule performance is mainly manifested in the number of molecule polar groups and the stability of the molecule polar groups. If the content of polar groups insufficient, then it will be unable to form effective protection for the metal. If the content of polar groups is excessive, then the corrosion inhibition efficiency will decrease. If the stability of the polar group is excessive, then the protective film from the corrosion inhibitor molecules is difficult to form or easily damaged and peeled off, and the corrosion inhibition effect is poor. When the stability of the polar groups decreases, the corrosion inhibitor molecules are likely to form an adsorption film with high density and adhesion; however, if the stability is insufficient, it will cause aggregation in the medium and thereby affect the corrosion inhibition performance. Therefore, when choosing corrosion inhibitor while ensuring its polarity, its solubility must be considered.

(2) Non-polar group

The influence of non-polar groups (such as hydrocarbon groups)

on corrosion inhibition performance is mainly reflected in two aspects: the length of the carbon chain of the non-polar groups and the structure of the non-polar groups. On the one hand, the longer the chain of nonpolar groups, the greater the solvation energy and molecule adsorption energy, the adsorption layer is thick and compact, and the corrosion inhibition effect is outstanding. However, the chain length of the non-polar group is inversely proportional to the corrosion inhibitor molecule solubility. The chain length should be determined according to the principle of Similar Solubility Parameters and the solvent solubility parameters. Otherwise, the solubility of molecules with too long chain length will decrease, unable to form a stable dense protective film.

On the other hand, if the number of branched chains of non-polar groups is excessive or/and the volume is huge, then the inhibitor molecules will have a huge volume that will increase the steric hindrance between the molecules. Hence, the corrosion inhibitor molecules cannot be closely arranged, and corrosive ions can penetrate the protective film, diffuse to the metal surface, and cause corrosion. For corrosion inhibitor molecules, an appropriate hydrocarbyl main chain should be a polynuclear group with short side chains, and the short side chain is mainly aromatic hydrocarbon or cycloalkyl; such structure can form a close arranged adsorption film.

8-2. Influence of Temperature

For most corrosion inhibitors, the adsorption force on metal surface decreases with the increase in temperature. The suitable temperature range varies for different corrosion inhibitors. Compared with oil-based cutting fluids with poor cooling performance, corrosion inhibitors are more suitable for water-based cutting fluids.

In addition to the above factors, the medium flow rate, PH, the concentration of medium salt ions, the hardness of water, the state of metal surface, and the interaction among different additives can also affect the corrosion inhibition.

8-3. Metal Suitability and Performance Comparison

Suitability between corrosion inhibitors and metals. Different corrosion inhibitors have different effects for different metal materials; if the corrosion inhibitor does not match the metal, it cannot provide protection and may even accelerate the corrosion. Table 11 summarizes the matching relationship between different metals and corrosion inhibitors in the cutting fluid. Different corrosion

Table 11. Corrosion inhibitor and metal type matching database

Metal substrate	Protective corrosion inhibitor	Corrosive corrosion inhibitor
Cast iron	Neodecanoic acid, Sebacic acid, Tall oil fatty acid, Dodecenyl succinic acid, Lauric acid, Undecanedioic acid, 6,6′,6″-(1,3,5-triazine-2,4,6-triyltriimino) trihexanoic acid	Phosphate ester corrosion inhibitor
	Amide corrosion inhibitor	
	N-octanoic acid monoethanolamine, Sebacic acid triethanolamine, Azelaic acid triethanolamine	
	Benzotriazole, Di-tert-butylated benzotriazole	
	Borate ester corrosion inhibitor	
Aluminum material	Molybdate corrosion inhibitor	Alkanolamine corrosion inhibitor
	Silicat corrosion inhibitor	
	Dodecenyl succinic acid silicat	
	Triethanolamine oleate, Azelaic acid triethanolamine	
	Phosphate ester corrosion inhibitor	
	Borate ester corrosion inhibitor	
Copper material	Thiadiazole corrosion inhibitor	Alkanolamine corrosion inhibitor
	Benzotriazole and its derivatives	
Carbide tools	Benzotriazole	Alkanolamine corrosion inhibitor
	Triethanolamine oleate, Triethanolamine nitrobenzoate	
Steel	Molybdate corrosion inhibitor	
	Tungstate corrosion inhibitor	
	Alkanolamine corrosion inhibitor	
	Borate ester corrosion inhibitor	
Magnesium material	Silicat corrosion inhibitor	
	Fatty alcohol polyoxyethylene ether phosphate ester	
	Triethanolamine oleate	

Table 12. Comparison of corrosion inhibitor properties

Corrosion inhibitor type	Corrosion inhibition performance	Environment friendly	Economy
Molybdate	****	***	*
Tungstate	****	***	*
Silicate	**	****	*****
Alkanolamine	*	**	*****
Carboxylic acid	**	****	****
Amide	***	****	***
Carboxylic acid salt	****	****	**
Thiadiazole	*****	*	*
Triazole	****	****	***
Phosphate ester	*****	**	*****
Borate ester	****	*****	**

inhibitors have different performance; therefore, Table 12 makes a horizontal comparison of various organic and inorganic corrosion inhibitors from the perspectives of corrosion inhibition, environmental protection and economy, after market research.

COMPOUND USE OF INORGANIC AND ORGANIC CORROSION INHIBITOR

Inorganic corrosion inhibitors mainly have disadvantages such as large dosage and expense. Organic corrosion inhibitors are widely used because of their low cost, environmental protection, and low dosage compared with inorganic corrosion inhibitors, and therefore are the main object of application and research in the field of cutting fluid. However, a single organic corrosion inhibitor is greatly affected by metal surface state, temperature and immersion time, inability to maintain stability, and corrosion inhibition performance in harsh environments. For some special machining fields, a single organic corrosion inhibitor cannot meet the demanding corrosion inhibition requirements [90]. Compounding organic and inorganic corrosion inhibitors can greatly enhance the corrosion

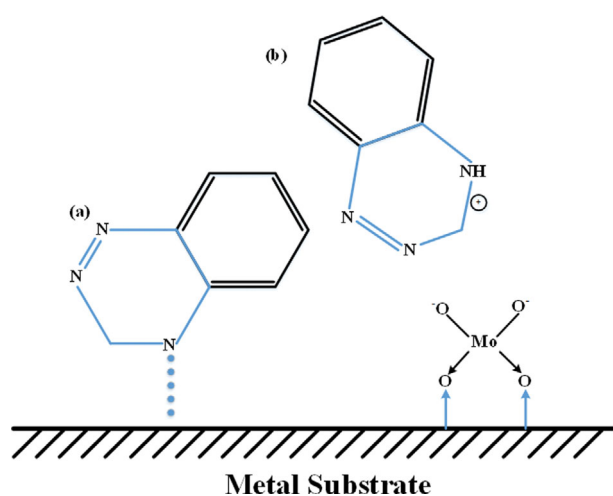**Fig. 29. Corrosion inhibition mechanism of Na₂MoO₄-BTA compounded system [59].**

inhibition performance and stability of the system while reducing the usage of both.

Zhou et al. [59] found that when benzotriazole (BTA) and sodium molybdate are compounded, the composition of the corrosion inhibitor film is mainly $FeMoO_4$ and BTA-Fe, as shown in Fig. 29. The composite structure improves the compactness of the $FeMoO_4$ corrosion inhibition film and promotes the conversion of FeOOH in carbon surface passivation film into stable Fe_2O_3, thus further enhancing the corrosion inhibition film stability. When the pH is 8.16-10, the corrosion inhibition efficiency reaches more than 99%, and the compound system requires a low concentration and has a high stability.

In 2016, Kim et al. [199,200] discovered the synergistic effect of nitrate and three kinds of ethanolamines on carbon steel in the tap water medium and found that the synergistic mechanism is due to tungstate forming an oxide film by oxidizing the surface of the metal to generate a passivation layer. Meanwhile, ethanolamines are adsorbed on the surface of spheroidized graphite to form a protective film. The two films work together to enhance the corrosion inhibition effect, and the principle is shown in Fig. 30. Electron attractive groups in ethanolamine inhibitor lead to a poor synergistic effect. For 100% corrosion inhibition effect, the dosage of a single ethanolamine corrosion inhibitor must be as high as 100 Kppm; however, after only 1 kppm nitrite+1 kppm monoethanolamine (MEA) is compounded, and the corrosion inhibition efficiency can reach 100%, and the stability of the system is significantly improved.

However, carcinogenic nitrosamines are produced when amines are mixed with sodium nitrite. In 2017, the synergistic effect of molybdate and MEA for carbon steel corrosion inhibition in tap water media based on the above principles was studied and a good corrosion inhibition effect was achieved by adding 1 kppm molybdate+1 kppm MEA. In addition, the compound system requires a low concentration and has a high stability. With the use of electron probe microscopic analysis instrument, the principle was confirmed to be in line with that from 2016 [201].

Gao et al. [202] found that in the solution with pH 11.00 and 0.5 M NaCl, the combination of Na_2WO_4 and hexamethylenetetramine (HMTA) according to a certain proportion can form a
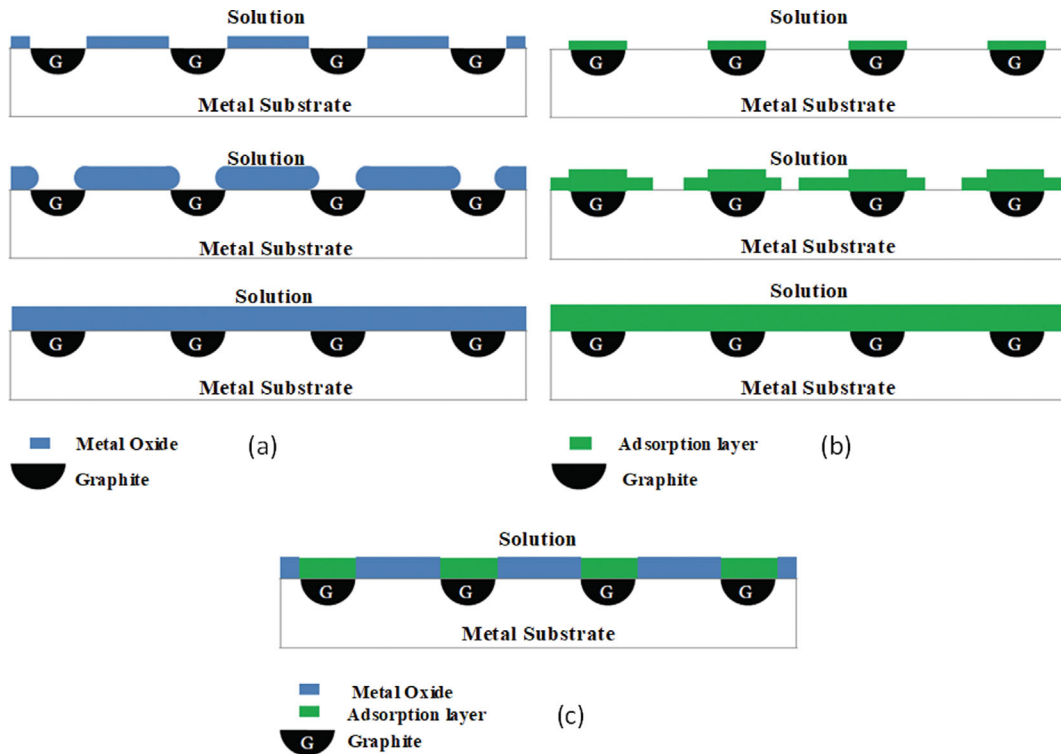
Fig. 30. New corrosion inhibiting mechanisms (a) nitrite single addition. (b) Ethanolamine single addition, and (c) co-addition of nitrite+ ethanolamines [199].

composite protective film on the steel surface to inhibit corrosion, and the corrosion inhibition efficiency reaches 97.1%. Inspired by Kim et al. [201], Lim et al. [203] found that after tungstate and MEA are compounded, tungstate forms an oxide film to act as a passivation layer by oxidizing the metal surface. Ethanolamine is then adsorbed on the surface of spheroidized graphite, thereby enhancing the rust resistance of nodular cast iron. Lin et al. [29] studied the synergistic corrosion inhibition effect of calcium ligno-sulfonate (CLS), molybdate, and stannate for carbon steel in the solution with pH 11.00 and 0.5 M NaCl and found that molybdate

and stannate can enhance the passivation film. Calcium, molybdenum/tin oxides, and hydroxides generate a deposited film. Finally, CLS is adsorbed on the outside of the steel surface to form a hydrophobic layer. The corrosion inhibition efficiency of the three-layer composite membrane reaches 94%, and the compound system requires a low concentration and has a high stability as shown in Fig. 31.

Hu et al. [204] studied the cooperative inhibition mechanism of Mannich base ($C_{15}H_{15}NO$) and sodium tungstate and found that Mannich base is first adsorbed on the metal surface to form a pro-
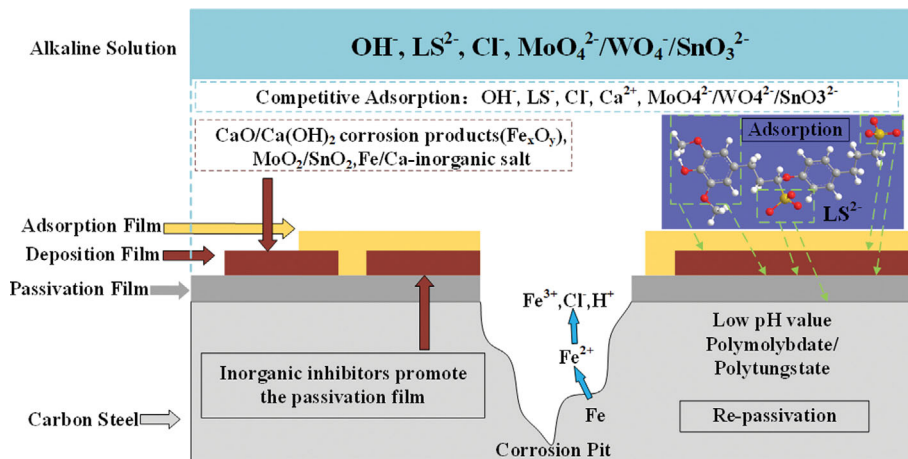
Fig. 31. Illustration of the inhibition mechanism [29].
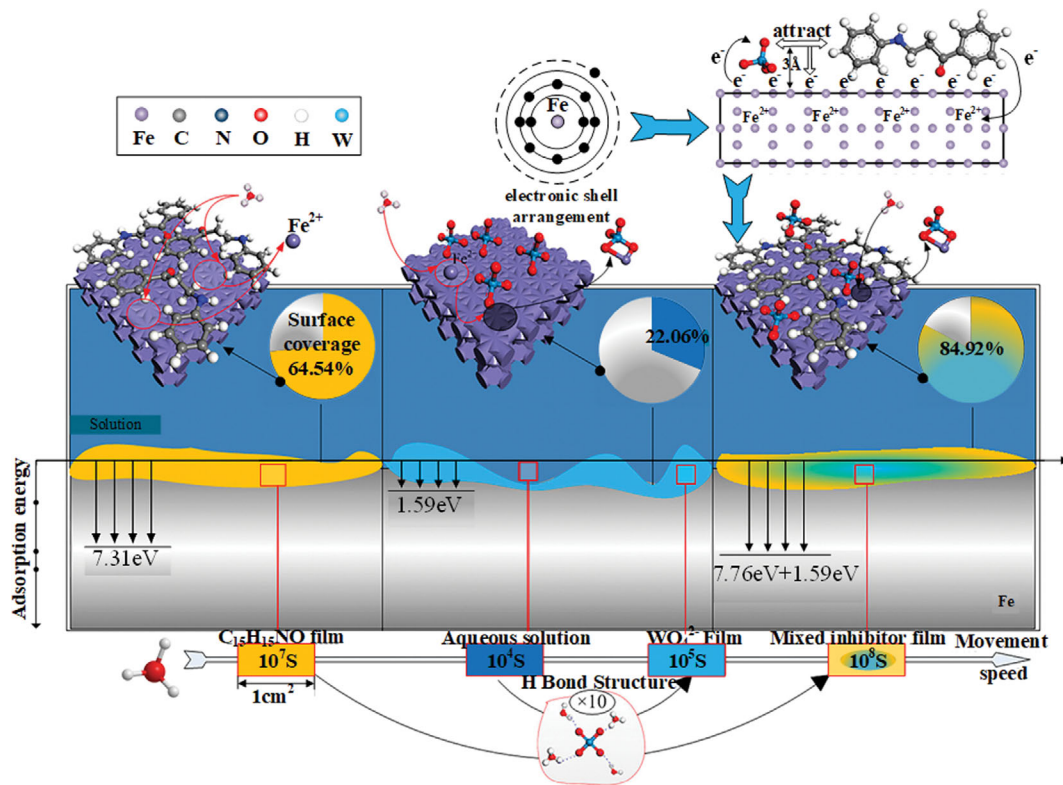
Fig. 32. Corrosion inhibition mechanism of $C_{15}H_{15}NO$- Na_2WO_4 compounded system [204].
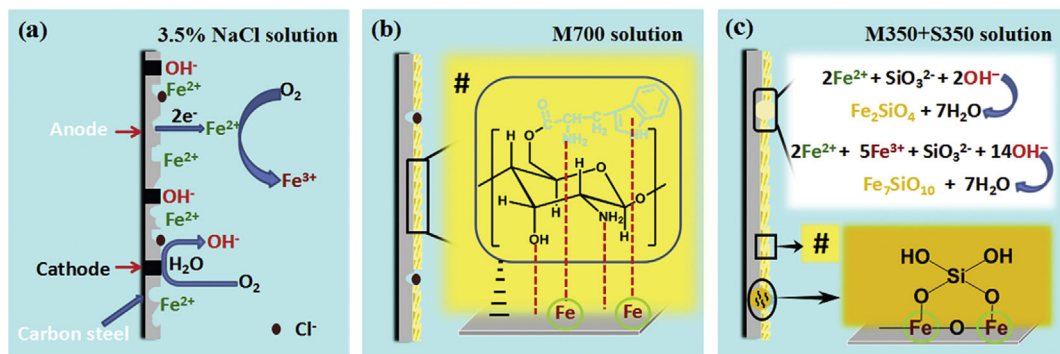
Fig. 33. Corrosion mechanism of carbon steel in 3.5 wt% NaCl solution (a) 700 ppm MCO solution (b) and 350 ppm MCO+350 ppm sodium silicate solution (c) [90].

tective film due to its high adsorption energy. Tungstate ions are then adsorbed in the gaps of the Mannich base protective film to form a tight film and form hydrogen bond groups with hydrogen ions, thus preventing corrosive ions to pass through the adsorption film and greatly reducing the number of corrosive ions close to the metal surface as shown in Fig. 32.

Carbon steel produces corrosion products in sodium chloride solution, including FeOOH, Fe_2O_3, and Fe_3O_4. The mechanism is shown in Fig. 33(a). Wang et al. [90] found when only add MCO (modified chitooligosaccharides), the corrosion inhibitor layer is unstable and the chloride ions leads to local corrosion. The reaction mechanism is shown in Fig. 33(b). After sodium silicate was added, the local corrosion was remarkably inhibited, as shown in

Fig. 33(c).

The mechanism includes two paths. One is the free silica ions diffuse to steel surface and may react with Fe^{3+}/Fe^{2+} and OH^- to produce insoluble silicate compounds deposited on the steel. The other is the oligomer formed by silica ion is hydrolyzed to form a protective film containing iron and silicon elements.

Ming et al. [94] prepared a water-based microemulsified aluminum alloy cutting fluid by compounding sodium silicate and boric acid monoethanolamine and found that the corrosion inhibition rate for aluminum alloy reached 97.49%. The combination of sodium dodecyl benzene sulfonate (SDBS) and Na_2SiO_3 has better corrosion inhibition effects than single use, SDBS adsorbed on the defects of the inhibition film; the combined system will produce a com-

posite precipitation film of silicate and magnesium hydroxide on the magnesium alloy surface, and the inhibitive efficiency can be improved to 95.3% [205].

After the inorganic and organic corrosion inhibitors are compounded, the corrosion inhibition performance and stability of the compound system are greatly improved. The corrosion inhibition mechanism after combination mostly follows the Filling Principle, that is, one type of inhibitor corrosion molecules will fill in the gaps in the protective film formed by another corrosion inhibitor, thereby synergistically enhancing the corrosion inhibition ability. However, current research on compound corrosion inhibition systems in cutting fluid field is limited. The use of compound corrosion inhibitors can be considered when the corrosion inhibition performance requirements are relatively strict and the processing environment is relatively harsh.

CONCLUSIONS AND OUTLOOK

This article focuses on the problems of metal corrosion caused by cutting fluids during metal processing and systematically introduces the classification, working mechanism, suitability, and influencing factors of corrosion inhibitors. Recent application and research progress of corrosion inhibitors in cutting fluids are also summarized. The main findings are as follows:

(1) Most inorganic corrosion inhibitors are oxidants that protect metal by forming an oxide film or precipitation film on the metal surface through oxidation. Concentration is an important factor affecting the performance of inorganic corrosion inhibitors. If the concentration is insufficient, then the metal is not protected and corrosion can even be accelerated. However, under special circumstances, some inorganic corrosion inhibitors are also invalid at high concentrations. Molybdate and tungstate have excellent corrosion inhibition effects on ferrous metals such as steel, and silicate is suitable for the protection of aluminum materials. The compound use of inorganic and organic corrosion inhibitors is the main research direction of inorganic corrosion inhibitors.

(2) The polar groups in the organic corrosion inhibitor molecules can be adsorbed on the metal surface, and the non-polar chains are aligned in the medium to form an adsorption film to protect the metal. The number and stability of polar groups should not be excessive, and the chain length of non-polar groups should be determined according to the principle of Similar Solubility Parameters. In most cases, the increase in temperature decreases the corrosion inhibition efficiency. Alkanolamine, amide is suitable for cast iron, carboxylic acid salt, and borate ester corrosion inhibitor can be used as a general additive, thiadiazole and triazole corrosion inhibitors are suitable for copper, and phosphate ester is suitable for aluminum.

(3) After the inorganic and organic corrosion inhibitors are compounded, the corrosion inhibition performance and stability of the compound system are greatly improved. The corrosion inhibition mechanism after the combination mostly follows the Filling Principle, that is, one type of inhibitor corrosion molecules will fill in the gaps in the protective film formed by another corrosion inhibitor, thereby synergistically enhancing the corrosion inhibition ability.

The recent application and research of corrosion inhibition technology in cutting fluid have achieved remarkable results, but some

limitations still exist. According to a systematic review, future research directions may focus on the following topics:

(1) Exploring the mechanism of corrosion inhibitor invalidity and accelerated corrosion by molecular dynamics, such as tungstate and molybdate invalidity, alkylamine corrosion for copper, aluminum, and carbide tools, and phosphate ester corroding cast iron.

(2) Separately classifying the effective components crucial in corrosion inhibition through methods such as high performance liquid chromatography-mass spectrometry or gas chromatography-mass spectrometry; further refining the correspondence among the types of corrosion inhibitors, applicable temperature, pH, and metal types; using the research results as a theoretical basis and introducing groups and elements with different properties into the same molecule through molecular design to study general-purpose green additives.

(3) Researching the suitability of corrosion inhibitor and base fluid through physical and chemical analysis to prevent precipitation, delamination, and other problem after compounding.

DECLARATIONS

Conflicts of Interest/Competing Interests

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

Availability of Data and Material

The datasets supporting the conclusions of this article are included within the article.

Code Availability

Not applicable

Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by [Zongming Zhou], [Xiaolin Nie], [Yun Chen], [Huajun Cao], [Bo Liu], [Naiqing Zhang], [Zafar Said], [Sujan Debnath], [Muhammad Jamil], [Hafiz Muhammad Ali], and [Shubham Sharma]. The first draft of the manuscript was written by [Haogang Li], [Yanbin Zhang] and [Changhe Li] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Ethics Approval

Not applicable

Consent to Participate and Publish

The authors declare that they participated in this paper willingly and the authors declare to consent to the publication of this paper.

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