

Tobacco Extracts as Pickling Inhibitors

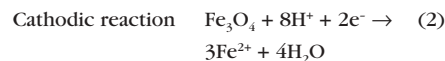
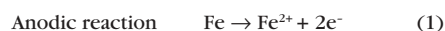
J.A. VON FRAUNHOFER, *Inhibitrol, Inc.*
GUY D. DAVIS, *DACCO SCI, Inc.*

Two tobacco extracts were tested and found to be effective inhibitors for 1008 steel (UNS G1008) in 10% sulfuric acid (H_2SO_4) and 4% hydrochloric acid (HCl). The precise inhibition mechanism is yet to be determined, but it appears to involve polarization of the cathodic reaction and passivation of the metal surface. Tobacco extracts are environmentally benign and come from a renewable source.

The removal of corrosion products, oxides, and mill scale from metal surfaces is a prerequisite before the metal undergoes forming, cold-rolling, or other mechanical treatment. Providing metals with a clean surface also is mandatory prior to electroplating, painting, vitreous enamel coating, and galvanizing. Although a variety of methods, including mechanical or abrasive cleaning, can be used to achieve clean metal surfaces, the most effective approach is acid pickling—either used alone or in conjunction with other pretreatments.

Acid Pickling

Removing corrosion products and mill scale from metal surfaces (notably steel) primarily involves reductive dissolution of surface oxides, which for magnetite would be:



It is likely that normal acid attack on the underlying metal ($\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$) facilitates scale removal by undermining the surface deposits. The evolved hydrogen may physically assist in undermining and lifting off surface oxides, but there might be some diffusion of atomic hydrogen into the substrate metal with subsequent embrittlement. The theory of acid pickling is well described elsewhere.¹

Pickling Acids

The most widely used acid for pickling of low-alloy steels is sulfuric acid (H_2SO_4), usually in 5 to 10% solution and often at elevated temperature (60 to 80°C). Electrolytic pickling, using impressed current, often is performed in such cases. However, anodic, cathodic, and alternating current polarization may be utilized as well, particularly for strip metal.

Increasingly, hydrochloric acid (HCl) (up to 10%) is used for pickling of steel despite its higher cost. HCl is more active than H_2SO_4 , and residual ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) on the metal surface washes off more readily than ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). Phosphoric acid can be used for steel pickling, but it is expensive and relatively slow-acting. Organic acids, typically dilute acetic and citric acids (CH_3COOH and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), often are used to remove calcareous deposits on steel. In addition, they are used on many nonferrous metals.

Aluminum and its alloys are commonly pickled in H_2SO_4 or nitric acid (HNO_3). Copper, copper-silicon alloys, and brass are pickled in H_2SO_4 or HCl. HCl is used for nickel-copper alloys, and sodium hydroxide (NaOH) solution is used for nickel-chromium alloys and aluminum bronze. Many of these solutions contain various additives to increase their efficiency (e.g., copper chloride [CuCl_2] for nickel-copper, hydrofluoric acid [HF] for copper-silicon,

and chromium trioxide [CrO₃] for aluminum alloys).

Pickling Inhibitors

During the pickling operation, thinner layers of scale and corrosion products are removed first so that areas of base metal are exposed and subjected to acid attack before the surface is clean. Inhibitors are customarily added to the acid to reduce, and ideally prevent, attack on the bare metal—although this eliminates the beneficial effect of hydrogen evolution on scale removal. Inhibitors offer the added advantages of reducing acid consumption and minimizing the formation of smut and carbonaceous deposits on the metal surface.

Ideally, the selected inhibitor is effective over long periods, does not reduce the pickling rate, reduces or prevents hydrogen absorption for steel substrates, and does not leave a surface film that may interfere with subsequent coating operations.

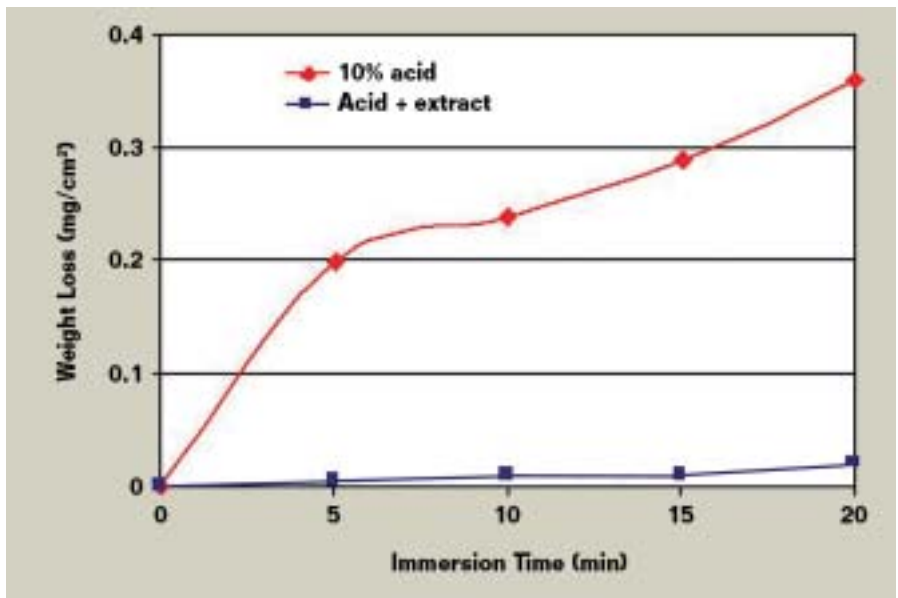
A variety of pickling inhibitors are available. Their inhibition efficiency, *I*, is expressed as:

$$I = \frac{CR_a - CR_i}{CR_a} \times 100\% \quad (3)$$

where *CR_a* is the corrosion rate in the plain acid and *CR_i* is that in the inhibited acid. An effective inhibitor provides 95% or better inhibition (*I* = 0.95), even in dilute solution. The electrochemical theory behind corrosion inhibition is discussed in numerous monographs.^{2,4}

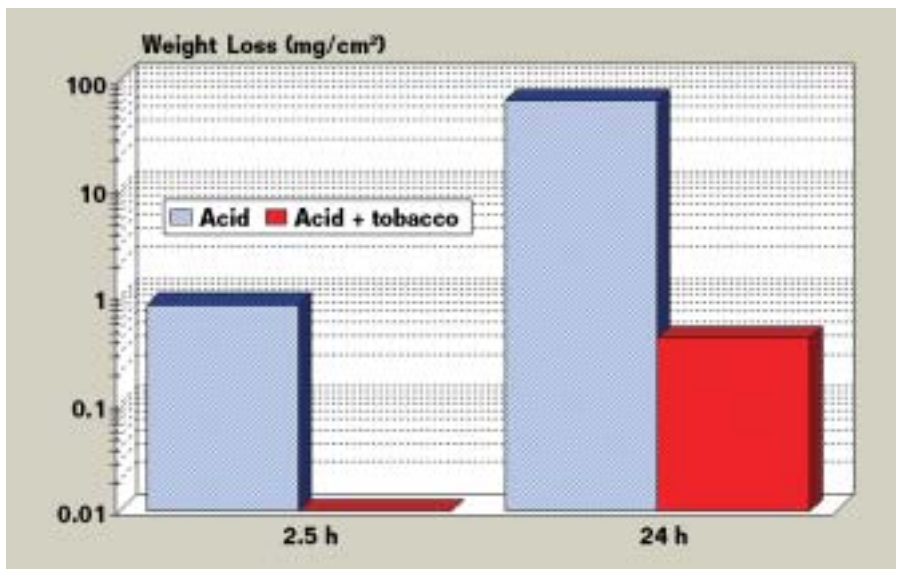
Inorganic inhibitors, typically the salts of metalloids such as arsenic and antimony, are effective for steel. Their inhibitive effect arises from deposition of the metal onto the steel surface. Because these metals are cathodic to iron and usually have a high hydrogen overpotential, they prevent discharge of hydrogen ions and block the normal Fe/H⁺ reaction. This blocking action, however, increases the diffusion of atomic hydrogen into the steel; a consequent increase in brittleness also

FIGURE 1



Corrosion of mild steel rods in 10% H₂SO₄.

FIGURE 2



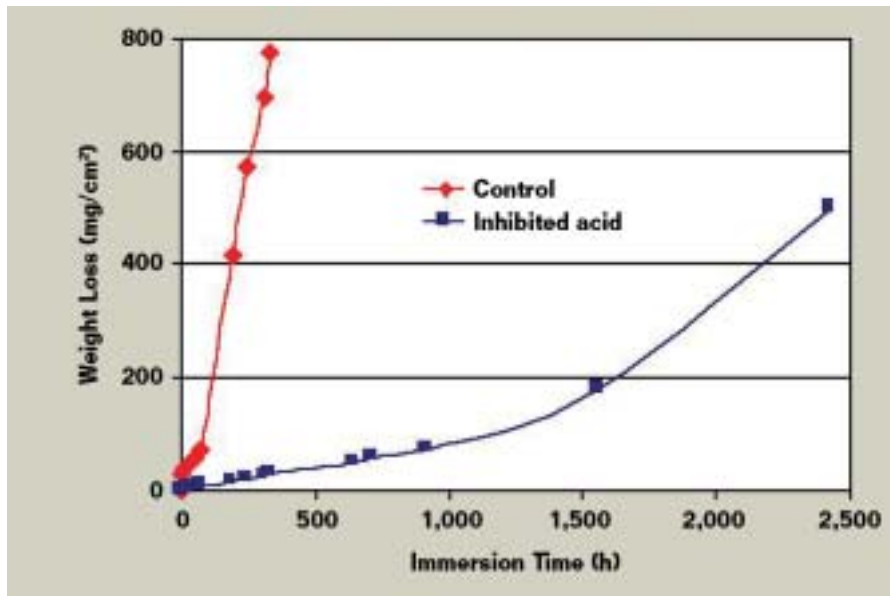
Corrosion of SAE 1008 cold-rolled steel in 10% H₂SO₄. Inhibitor efficiency: *I*_{2.5h} = 98.8%; *I*_{24h} = 99.4% (note logarithmic scale).

occurs. For this reason, inorganic inhibitors seldom are used on a commercial scale. Organic inhibitor use is the norm.

Various organic compounds are used in pickling acid inhibition. They predominantly contain sulfur, nitrogen, or oxygen atoms, with sulfur compounds being favored for H₂SO₄ and

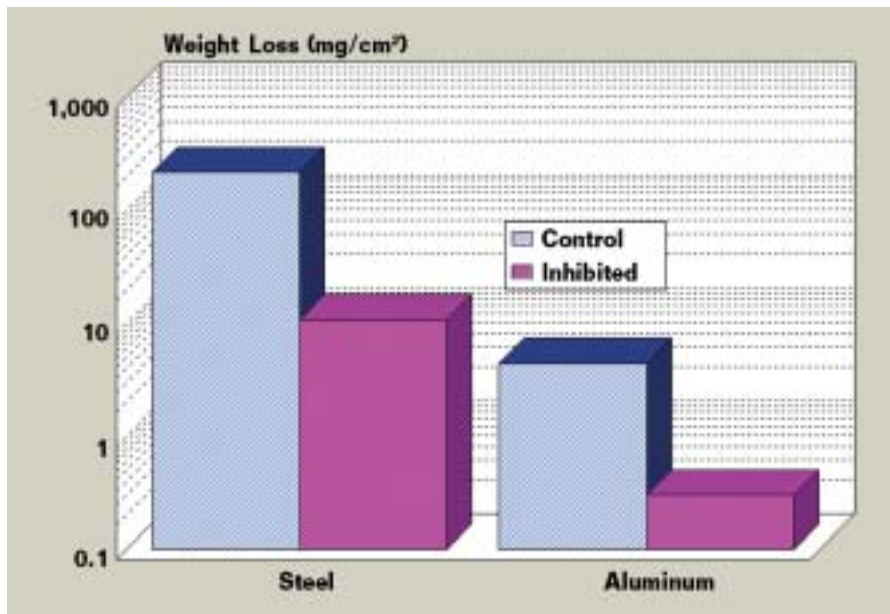
nitrogen compounds for HCl solutions.^{2,4} It appears that synergistic effects operate with these inhibitors because mixtures of sulfur and nitrogen compounds are more effective than either type alone. Furthermore, synergistic effects apparently occur when there are chlorides present in H₂SO₄ pickling media.

FIGURE 3



Long-term corrosion of SAE 1008 cold-rolled steel in 10.6% H₂SO₄.

FIGURE 4



Weight loss of steel and aluminum in 4.1% HCl at 1 h. Inhibitor efficiency: $I_{\text{steel}} = 93.2\%$; $I_{\text{aluminum}} = 95.1\%$ (note logarithmic scale).

The most widely used sulfur compounds are various substituted ureas, thioureas, thiazoles, sulfoxides, sulfides, and mercaptans. Nitrogen compounds typically are amines and imines, amino acids, proteins, hetero-

cyclics, and quinolines. Acid inhibitors based on oxygen compounds include a variety of alcohols, carbonyl compounds, acetylenics, dihydric alcohols, and proteinaceous compounds such as gelatin.

Tobacco Extracts as Pickling Inhibitors

The tobacco plant contains at least 4,000 chemical compounds, including such electrochemically active compounds as alcohols, polyphenols, carboxylic acids, nitrogen-containing compounds, and alkaloids.⁵ These components may be leached by water from tobacco plants, and they have been shown to be efficient corrosion inhibitors in a variety of media.^{6,9} Tobacco extracts are biodegradable and environmentally benign, with minimal health and safety concerns. Derived from a renewable biosource, they are cost-effective. Given the diversity of compounds within tobacco extracts, identifying individual active inhibitive components is very difficult. Therefore, the focus of research and development efforts has been to develop an inexpensive natural extraction product that effectively inhibits mineral acids.

Two extraction procedures were used for the present study. In the first (and simpler) procedure, dilute mineral and organic acids were directly extracted from scrap tobacco plant twigs and stems. The procedure yielded a concentration of ~5% tobacco extract in solution. In the second approach, dried and cured tobacco leaves were extracted into water to yield a 0.3% aqueous extract solution. The solution was used to dilute the appropriate mineral or organic acid into the working concentration.

The corrosion test specimens were SAE 1008 (UNS G1008) steel and 3105 (UNS A93105) aluminum panels. All specimens were weighed to 0.1 mg.

Results

Figure 1 shows the weight loss of mild steel through acid attack in plain 10% H₂SO₄ and inhibited 10% H₂SO₄. The acid was inhibited by direct leaching of dried scrap tobacco twigs and stems with the acid. The metal

exposed to the inhibited acid showed minimal weight loss over 20 min; however, there was marked attack in the plain acid. The specimens in plain acid showed the classic blackened surface and quasi-pitting, but the metal immersed in the inhibited acid remained bright and blemish-free. Similar results were obtained with SAE 1008 cold-rolled steel over longer immersion times; the inhibitor efficiencies were 98.8 and 99.4 at 2.5 and 24 h, respectively (Figure 2). Figure 3 shows differences in metal loss in plain and inhibited acids with extended exposure. Complete dissolution of the steel occurred within 350 h in the plain acid, whereas protection was still evident after 2,500 h in the inhibited acid. The inhibited solution was prepared by diluting concentrated H_2SO_4 with 0.3% aqueous tobacco solution.

Comparable inhibition of acid attack in 4.1% HCl was noted for both steel and aluminum. Figure 4 shows the dissolution that occurred at 1 h, with inhibitor efficiencies of 93.2 and 95.1% for steel and aluminum, respectively. Figure 5 shows the long-term attack on steel by dilute HCl, with complete dissolution of steel occurring within 500 h.

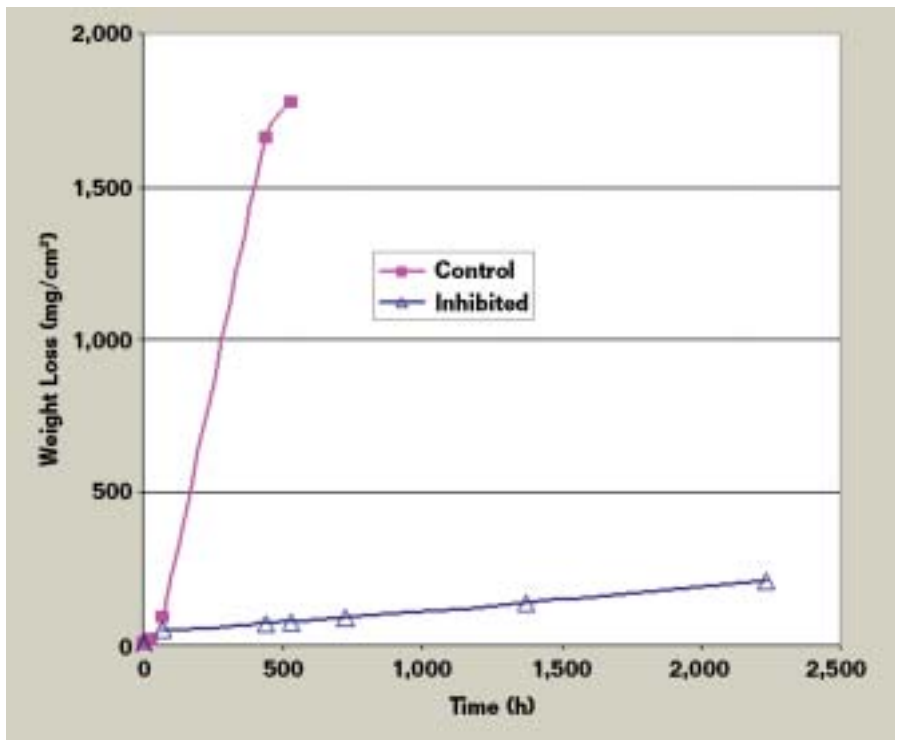
Tobacco extracts likewise were found to be effective inhibitors in dilute acetic and citric acid solutions (Figure 6). The inhibition efficiency at 20 h was 62.7% for steel and 82.4% for aluminum. Inhibition efficiency for steel in 2.2% citric acid after 1,800 h was 92.8 and 54.1% for aluminum.

There was no evidence of significant surface deposition of matter on the exposed metal surfaces in the acid media. Further, there were no indications of steel embrittlement arising from hydrogen diffusion into the substrate metal.

Discussion

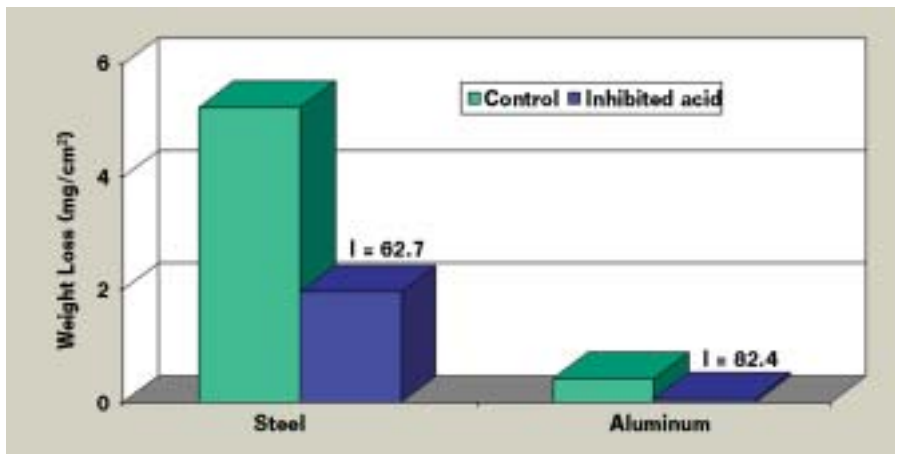
The data demonstrate that tobacco extracts, even at low addition levels, are effective corrosion inhibitors for steel and aluminum in dilute mineral

FIGURE 5



Long-term corrosion of SAE 1008 cold-rolled steel in 4.1% HCl.

FIGURE 6



Dissolution of steel and aluminum in 11% acetic acid solution after 20 h.

and organic acids. Tobacco extracts have been shown to be effective in many different acids and with a variety of metals.^{8,9} Other work¹⁰ indicates that effective inhibition also occurs in high-pH media.

These findings indicate that an environmentally benign, effective inhibitor can be obtained from a renewable

biosource. The precise mechanism of corrosion inhibition has yet to be determined, but preliminary studies suggest that it involves both polarization of the cathodic reaction and passivation of the metal surface. This dual action is unsurprising given the complexity and great number of electroactive species present in tobacco

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extracts. Nevertheless, it does account for the effectiveness and wide pH range of action. Because the inhibitor employs scrap material and tobacco leaf not meant for human consumption, raw materials cost is low.

Acknowledgments

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J. ANTHONY VON FRAUNHOFER is President of Inhibitrol, Inc., 11867 Sherbourne Drive, Timonium, MD 21093. He has published extensively in the fields of chemistry, corrosion, and biomaterials science. He is the Director of Biomaterials Science at The University of Maryland. He has an M.S. and Ph.D. in metallurgy, is a Fellow of the Royal Society of Chemistry and ASM International, and is a 2-year member of NACE.

GUY D. DAVIS is a Principal Scientist at DACCO SCI, Inc., 10260 Old Columbia Road, Columbia, MD 21046. He has more than 20 years of experience in basic and applied research and problem-solving. His research interests include adhesive bond formation and durability, surface treatments, corrosion inhibition, and corrosion sensing. He has a Ph.D. in materials science. He received the William Blum Award from the Electrochemical Society, is a Robert L. Patrick Fellow of The Adhesion Society, is Fellow of the American Vacuum Society and ASM International, and is a NACE member. *MP*