

The Use of Tobacco Extracts as Corrosion Inhibitors

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ABSTRACT

Extracts of tobacco plants show considerable promise as environmentally acceptable corrosion inhibitors. Use of extracts obtained from stems and twigs, as well as leaves, show significant corrosion inhibition during immersion of aluminum or steel in saline solutions and immersion of steel in strong pickling acids. In several cases, the inhibition is greater than that provided by chromates and is provided over a wide range of extract solution concentrations. When steel was treated in sulfuric acid with tobacco extract to remove mill scale and rust, the steel emerged bright and shiny. When treated in sulfuric acid alone, the steel was blackened and pitted. The tobacco extracts provide corrosion protection from a renewable resource with little or no environmental impact. The use of waste plant material enables an inexpensive source of corrosion inhibitors.

INTRODUCTION

There is a continual need to develop environmentally friendly corrosion inhibitors to replace the traditional inorganic corrosion inhibitors, such as chromates and lead, which have significant health, safety, and environmental concerns. Both are listed as persistent, bioaccumulative, and toxic (PBT) chemicals.¹ Because PBT chemicals do not readily break down or decrease in potency in the environment, they accumulate and have greater potential to cause long-term human health or ecological problems. They continue to be an environmental concern long after they are used and the nation's goal is to reduce the generation of these chemicals in hazardous waste by 50% by 2005 with source reduction and recycling, as intended by the Resource Conservation and Recovery Act (RCRA), Clean Air Acts, the Pollution Prevention Act, and the Hazardous and Solid Waste Amendments (HSWA), among others. Thus, new, ef-

fective inhibitors that are safe and environmentally benign must be found.

Extracts from tobacco plants show excellent corrosion inhibition properties for several metals.²⁻⁴ The tobacco plant is a virtual chemical factory with over 4,000 compounds being reported by the USDA. Tobacco is currently being evaluated as a production system for antibiotics, sugars, industrial enzymes, and anti-cancer and AIDS compounds.⁵⁻⁹ Some of the tobacco constituents show remarkable corrosion inhibitive properties. Tobacco extracts represent a major new initiative in the corrosion inhibition market with the following potential advantages:

- Low cost and high effectiveness
- Environmentally acceptable
- Low toxicity
- Readily available and renewable.

At the beginning of the twentieth century and earlier, biomass, in the form of wood, was the major source of organic chemicals in the US. It is projected that in the coming years, biomass will again come to be viewed as an important, renewable feedstock for the wide range of needed chemicals. Biomass has a potential advantage over petrochemical feedstocks: it already contains a wide range of naturally-synthesized chemical compounds that can be extracted by straightforward processes, obviating the need for complex manufacturing syntheses from basic, petroleum-derived, building blocks. Tobacco should be viewed as an incredibly rich source of complex chemicals. Extraction of chemicals from biomass is a more attractive approach than merely using biomass to make fuels as the latter destroys these complex molecules.

Corrosion inhibitors have been studied for many years [see, e.g., Ref. 10 and 11]. Many types of organic compounds have been found to act as inhibitors [see, e.g., Ref. 12 and 13], but most of these compounds have remained as laboratory data. One reason seems to have been that the cost of manufacture of these compounds is generally too high for the corrosion market. In contrast, tobacco extracts can be prepared at very low cost, especially if simple extract procedures can be used and scrap plant parts can be used without curing.

Effective adsorbing inhibitors include aliphatic and aromatic amines, sulphur-compounds such as thiourea and substituted thioureas, carboxylic acids and their salts, aldehydes and ketones as well as numerous other organic substances. These substances exist either in the charged state or as neutral entities that are readily polarizable. Thus, in addition to the high surface adsorbability of N-, S- and O-compounds, the metal surface charge may be expected to affect adsorption. Synergistic (and antagonistic) effects are often found with mixtures of inhibitors and these effects may be related to the charge in the electrical double layer (edl) present between an electrode (the metal surface) and its environment.

Tobacco products contain a high concentration of alkaloids, fatty acids and N-containing compounds,¹⁴ many of which might be anticipated to exhibit electrochemical activity. Some 4,000 individual constituents have been identified in tobacco but electrochemical activity, requiring the presence of polarizable nitrogen, oxygen and sulphur atoms, is likely only with a limited number of constituents. Polynuclear aromatic hydrocarbons also may be electrochemically active due to their fused benzene ring system with its attendant charge dislocation. These tobacco constituents with anticipated electrochemical activity include terpenes, alcohols, polyphenols, carboxylic acids, nitrogen-containing compounds, and alkaloids. Although there are a few reports on the inhibitive properties of compounds that bear some resemblance to the constituents of tobacco, namely organic amines, 3-amino-5-heptyl-1,2,3-triazole (AHT), benzoyl allyl alcohol, pyrazole derivatives and macrocyclic compounds, no direct parallels can be drawn with this present study.¹⁵⁻¹⁸

EXPERIMENTAL

Several different varieties of tobacco were evaluated in this study: NC129, KY171, MD609, B005, and Little Crittenden. Cured leaves, dried leaves, stems and twigs, and tobacco dust were tested to determine if the part of the plant or state of cure was important. Initial studies also included commercial tobacco products. Extractions were generally achieved via aqueous solutions. Solution concentrations were obtained by weighing the solution, boiling off the water, and weighing the residue.

Metal panels were 1008/1010 cold-rolled steel and 3105 H24 aluminum Q-panels. Copper or brass was used to form a galvanic couple with aluminum or steel in some cases. Solutions were 1-3% NaCl. In some cases, potassium chromate or sodium dichromate was used as control inhibitors for comparisons. Other experiments included immersion in strong acids, such as those used in pickling treatments.

Initial work included measuring galvanic current from metal couples using a zero-resistance ammeter (ZRA). Weight loss measurements were also occasionally performed. Subsequent work included measuring corrosion currents from potentiodynamic polarization using an EG&G (Perkin Elmer) 273 potentiostat.

RESULTS AND DISCUSSION

The initial study compared the effects of 1% NaCl solution, 1% saline containing extracts from commercial tobacco products and 1% saline containing 1% of potassium chromate on several galvanic couples. Corrosion inhibition is denoted by a reduction in current density. Figure 1 (left) clearly shows that a simple aqueous extract of chewing tobacco leached out a powerful corrosion inhibitor, one that appeared to be more effective and more rapid in its action for the copper-steel galvanic couple than the established anodic passivating inhibitor, potassium chromate. ZRA studies on galvanic cells established between other metal pairs, including copper and aluminum, mild steel and aluminum, and brass and aluminum also demonstrated inhibition of corrosion through addition of aqueous tobacco product extracts (Figure 1 and Figure 2). In the case of couples involving aluminum, the corrosion current density decreased by one to almost three orders of magnitude compared to the uninhibited saline solution and a

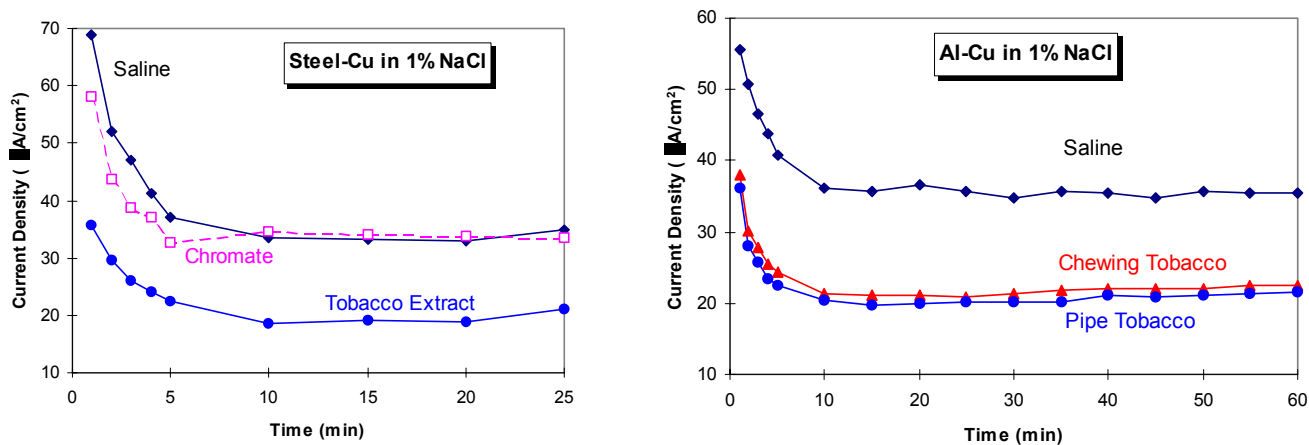


Figure 1. Corrosion current density of the steel-Cu (left) and Al-Cu (right) galvanic couple immersed in 1% NaCl solution with and without extracts from commercial tobacco products. The steel-Cu couple also includes potassium chromate.

factor of 2-5 compared to the chromate solution.

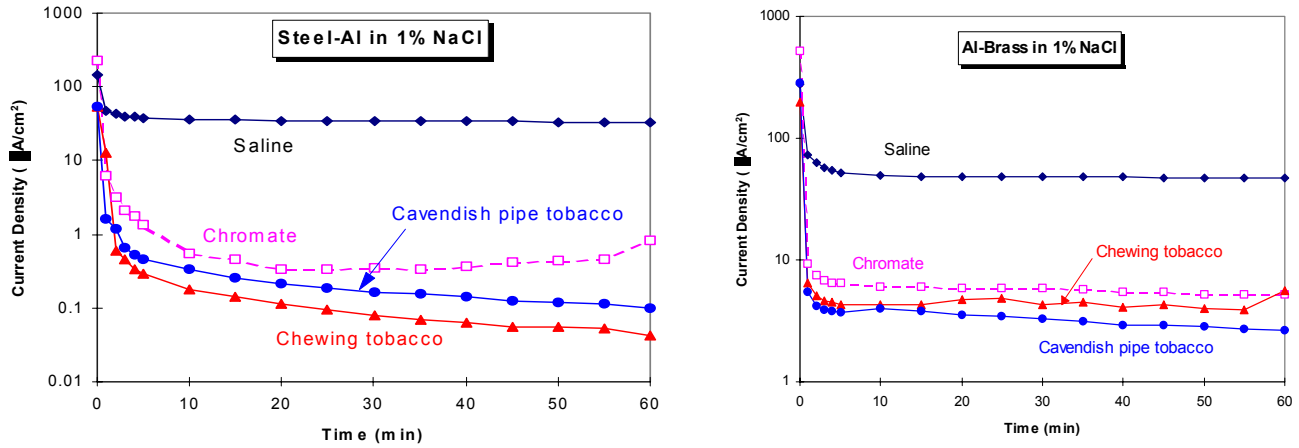


Figure 2. Corrosion current density of the steel-Al (left) and Al-Brass (right) galvanic couple immersed in 1% NaCl solution with and without extracts from commercial tobacco products. Also shown are results with a potassium chromate solution.

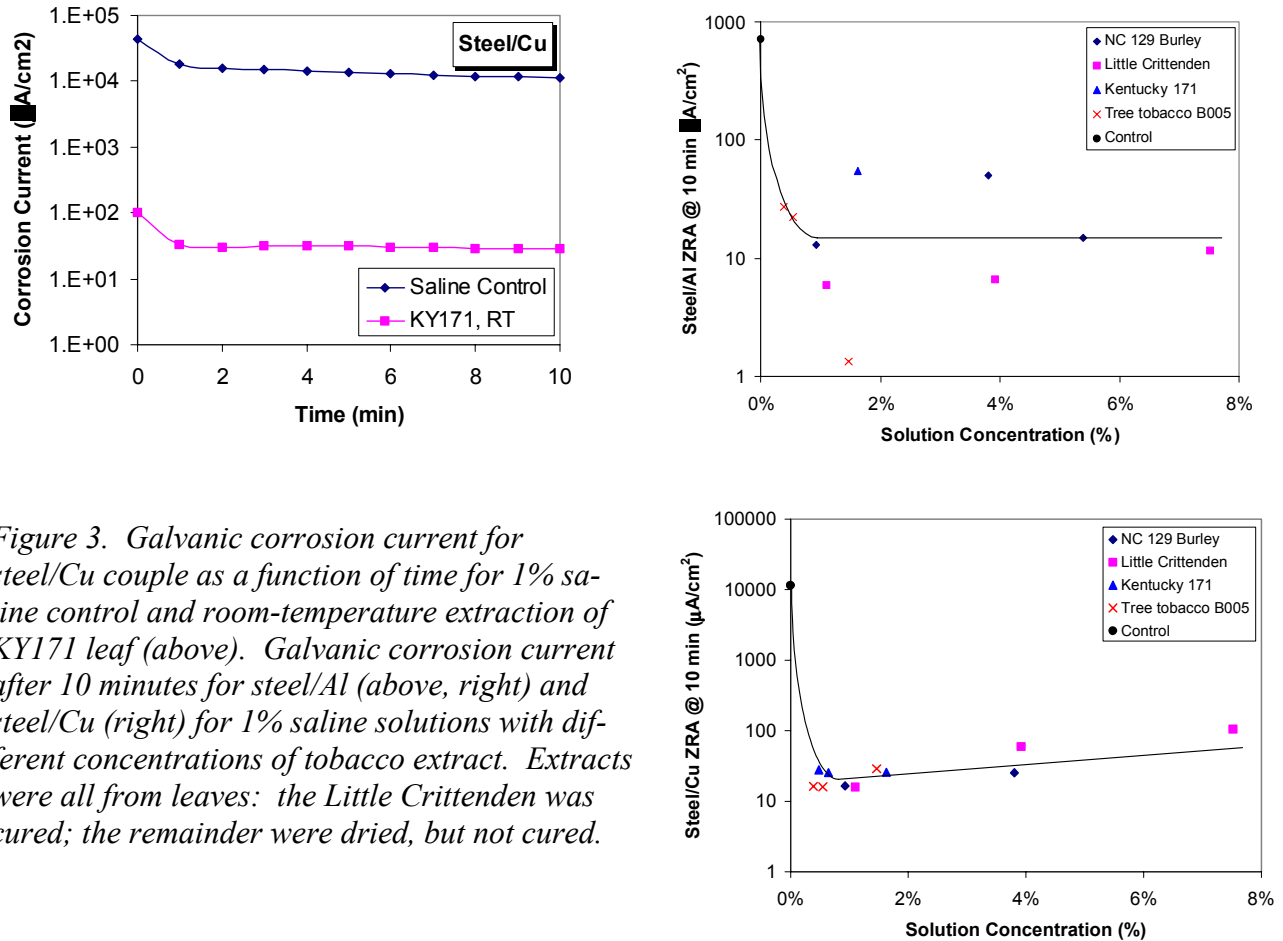


Figure 3. Galvanic corrosion current for steel/Cu couple as a function of time for 1% saline control and room-temperature extraction of KY171 leaf (above). Galvanic corrosion current after 10 minutes for steel/Al (above, right) and steel/Cu (right) for 1% saline solutions with different concentrations of tobacco extract. Extracts were all from leaves: the Little Crittenden was cured; the remainder were dried, but not cured.

Extracts of “raw” and cured tobacco were also evaluated. Typical ZRA data, giving the galvanic corrosion current between the two metal couples, is shown in Figure 3, upper left. Corrosion currents for different tobacco extract solutions are given in Figure 3, right. These results show a reduction factor of ~50 in the corrosion current for the steel/Al couple (top) and a reduction of a factor of ~400 in the corrosion current for the steel/Cu couple (bottom).

The results indicate that the corrosion current is largely independent of tobacco variety and the state of the leaves (cured vs dried). The later point is important as cured leaves are much more expensive as raw materials than dried leaves. Other results (reported below) indicate that waste stems and twigs are also effective. There is a strong dependence on solution concentration at very low levels (<0.025%), but that greater additions of tobacco do not appear to affect the corrosion current very much.

These conclusions were verified with the use of potentiodynamic polarization studies on aluminum as shown in Figure 4. No dependence on tobacco type or plant part (leaf or stem) is seen. At extract concentrations greater than ~0.1%, the tobacco provides inhibition very similar to that of sodium dichromate (0.1%). At lower concentrations (0.01-0.05%), the corrosion rate begins to increase, but still is more than an order of magnitude less than the control except for the 0.01% solution. The results indicate very wide process windows regarding the extraction process and plant variables.

Other experiments showing the effectiveness of tobacco extracts in reducing the corrosion occurring in different acid solutions were also very successful in demonstrating the inhibitive nature of the extract in more aggressive environments. Two different types of measurements in 5% solutions of acetic acid were made: weight loss and current induced by a metallic couple. The weight loss measurements are shown in Figure 5 for aluminum. In this case, the corrosion rate is reduced to ~20% of the uninhibited solution. No attempt was made in these experiments to optimize the solution concentration or other parameters.

More impressive is the reduction in galvanic current between the brass and copper couples in acetic acid that was provided by the tobacco extract as shown in Figure 6. After two minutes, the galvanic current was at or below the limit of sensitivity of the ammeter used in this experiment. During most of the time, the current in the acidified tobacco solution was less than 1% of the uninhibited acid. Integration over this period shows that the tobacco reduced corrosion by a factor of more than 60 (based on the limits of the ZRA).

Other work has been performed on inhibition of 10% sulfuric acid, a medium commonly used in the metal finishing and metal processing industries for descaling of steel prior to electroplating, painting and other surface coating procedures as well as prior to most metal working operations. Scrap burley twigs

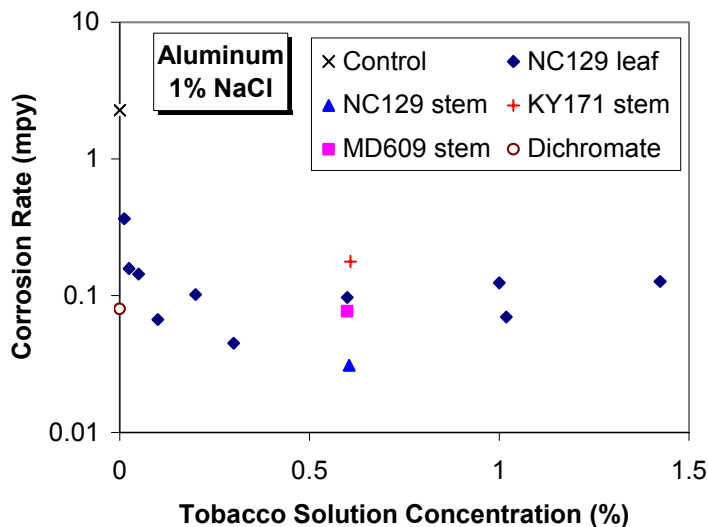


Figure 4. Corrosion rate for aluminum as a function of tobacco extract concentration in 1% NaCl solution. Also shown are the corrosion rates for saline solutions with no inhibitor and with 0.1% sodium dichromate.

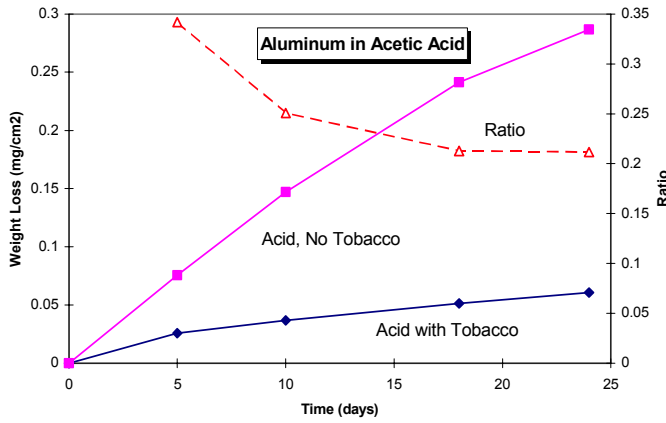


Figure 5. Weight loss measurements of aluminum as a function of time immersed in 5% acetic acid with and without 5% tobacco extract.

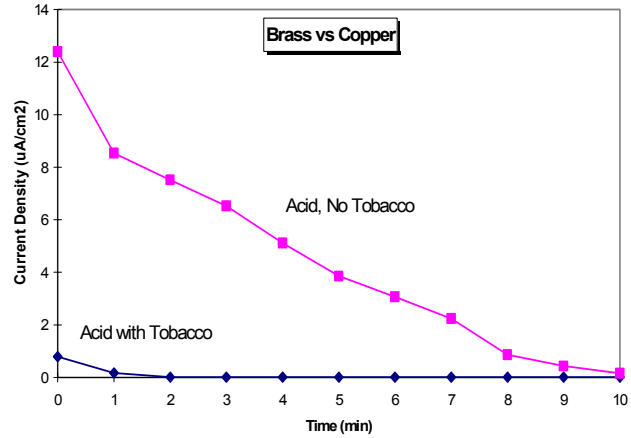


Figure 6. Current density of brass/copper galvanic couple in acetic acid with and without the tobacco extract.

and stems, remaining after stripping leaves and shoots for processing into tobacco products, were digested in 10% H₂SO₄ solution to provide a 5% extract concentration. Mild steel was then immersed in plain acid and the acid-burley extract for 5-minute intervals up to a total of 20 minutes, weight changes being recorded after each 5-minute period. The weight loss data are presented in Figure 7. The end result is a clean metal without rust or mill scale suitable for further processing while those from the untreated acid were blackened and pitted from the acid (Figure 7). This work clearly demonstrates the inhibitive effect of burley twigs and stems, materials that are discarded during tobacco processing.

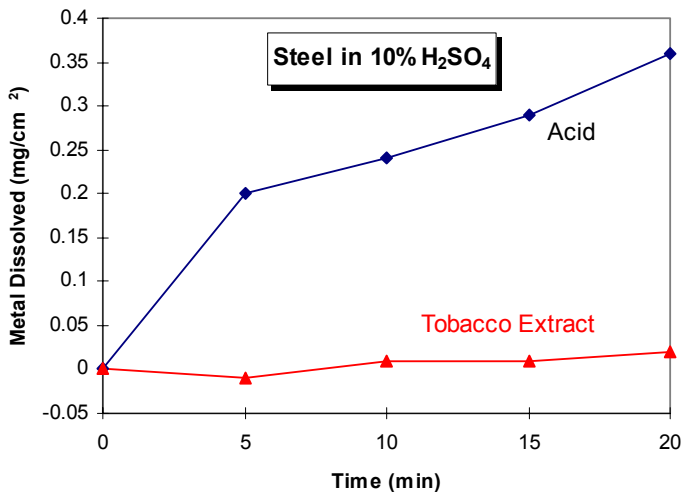


Figure 7. Attack on steel by 10% sulfuric acid with and without tobacco extract. Left: weight loss; right: steel rods after immersion.

CONCLUSIONS

Extracts from tobacco plants are very effective in reducing corrosion of aluminum and steel, both individually and in galvanic couples with each other or with copper/brass, in saline solutions. In many cases, the inhibition is even greater than that provided by chromates. The tobacco extracts appear to be effective over a wide range of solution concentrations, as low as 100 ppm. The extract also works in acidic solution and can prevent corrosion during descaling processes.

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REFERENCES

- ¹ Environmental Protection Agency, Environmental Fact Sheet EPA530-F-98-028 "EPA Releases RCRA Waster Minimization PBT Chemical List," November, 1998
- ² von Fraunhofer, J.A., Inhibiting corrosion with tobacco. *TEST Engineering and Management* **57**(3), 10-12 (1995).
- ³ von Fraunhofer, J.A., Tobacco Extract Composition and Method, U.S. Patent 5,435,941 (1995).
- ⁴ von Fraunhofer, J. A., *Advanced Materials and Processes* **158** 33, (2000).
- ⁵ Danehower, D.A., et al, "Tobacco as a Biochemical Resource: Past, Present, and Future," in *Biochemical Active Natural Products: Agrochemicals*, H.G. Cutler and S.J. Cutler, ed. (CRC Press, 1999).
- ⁶ Kusnadi et al., "Production of Recombinant Proteins in Transgenic Plants: Practical Considerations," *Biotech. Bioengr* **56**, 473 (1997).
- ⁷ DeJong, D.W., and J.A. Saunders, *Beit. Tabak. Internat.* **13** 139-149 (1986).
- ⁸ Kung, S.D., J.A. Saunders, T.C. Tso, D.A. Vaughan, M. Womack, R.C. Staples and G.R. Beecher, *J. Food Science* **45** 320-327 (1980).
- ⁹ *Messenger-Inquirer*, Louisville, KY, October 6, 1992.
- ¹⁰ Nathan, C.C., ed., *Corrosion Inhibitors*, National Association of Corrosion Engineers, Houston, TX, 1973.
- ¹¹ Hausler, R.H., ed., *Corrosion Inhibition - Theory and Practice*, National Association of Corrosion Engineers, Houston, TX, 1988.
- ¹² Craig, B.D., *Fundamental Aspects of Corrosion Films in Corrosion Science*, Plenum, 1991.
- ¹³ Trabenelli, G., and V.Carassiti, *Adv. Corrosion Science* **1**, 147-228, (1970).
- ¹⁴ World Health Organization, *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Volume 37: Tobacco Habits Other than Smoking; Betel-Quid and Areca-Nut Chewing; and Some Related Nitrosamines*, September 1985, International Agency for Research On Cancer.

¹⁵ Harrop, D., Chemical Inhibitors for Corrosion Control. in: *Chemical Inhibitors for Corrosion Control* ed. B.G. Clubley, Roy. Soc. Chem. Special Publication No. 71, Cambridge (1990).

¹⁶ Rudresh, H.B., and S. M. Mayanna: *Brit. Corrosion J.* **12** 54 (1977).

¹⁷ Rudresh, H.B., and S. M. Mayanna: *J. Electrochem Soc.* **4** 109 (1982).

¹⁸ Shih, H.C., R. J. Tzou, Y. N. Chen, Y. S. Lee: *Corrosion* **46** 913 (1990).