Reprinted From Electrochemical Technology
Vol. 5, No. 3-4, Mar.-Apr. 1967
Printed in U. S. A.

A Possible Role for Sulfate Reducers in the Corrosion of Aluminum Alloys

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Evidence was obtained for the presence of sulfate-reducing bacteria (Desulfovibrio sp.) in pits of an epoxy-topcoated aluminum alloy (7178) tank, and in tubercles and pits in a similar tank coated with Buna N. The sulfate-reducing bacteria were found in tubercles in association with *Pseudomonas aeruginosa* and *Cladosporium* sp. This association of microorganisms in developing oxygen concentration cells is discussed.

In the past few years, serious corrosion of aluminum alloys in integral fuel tanks and associated fuel system components has been a problem in turbine-powered aircraft utilizing hydrocarbon jet fuels. The corrosion has been associated with microbial contamination of the fuels (1-3). Most of the corroded fuel tanks were topcoated with a Buna-N phenolic resin. This material appears to be quite susceptible to microbial attack.

Development of Tubercles

In order to simulate topcoating deterioration and corrosion in the laboratory, several test tanks were fabricated from the same aluminum alloy used in integral wing tanks and were coated with various topcoatings. An artificial water-bottom was inoculated with a composite water-bottom from Ramey Air Force Base and overlaid with JP-4 fuel. Microbial problems, contamination problems, and corrosion were particularly acute at that base.

Blistering of the topcoatings and corrosion were noted in several of the tanks after they had been incubated for 90 days at 32°-35°C. No blistering or corrosion in the form of pits was observed in any of the tanks that had not received the inoculum or had received a Seitz-filtered inoculum (to remove the microorganisms). Two small, light-tan tubercles were observed on the bottom of one of the tanks. This particular tank, with internal dimensions of 5½ in. wide by 15 in. long and 2⅞ in. deep, was made of 7178 Allodyne-treated aluminum alloy and coated with No. 1039 epoxy resin. The water-bottom consisted of 90% by volume of sterile dilute (30%) Bushnell-Haas medium (4), with NH_4NO_3 as the nitrogen source, and 10% by volume of a composite of water-bottom samples from bulk storage tanks at the Air Force base. This water-bottom was overlaid with Ramey Air Force Base JP-4. Under u.v. light, these two tubercles, as well as the areas around them, showed a faint greenish fluorescence.

Examination of Tubercles

Examination of the tubercle shown in Fig. 1 revealed it to have the form of a small volcano. This view shows the crest of the tubercle removed and lying on its side. A small hole is visible through which small gas bubbles emerged. Considerable evolution of gas occurred during the photographing of this tubercle as a result of the intense heat from the lamps. A pit was found underneath the tubercle, ca. 2.3 mm in diameter and 0.5 mm deep.

Microscopic examination of the tubercle showed numerous fungal filaments, many rod-shaped bacteria, several spiral and comma-shaped organisms, and a considerable number of various irregularly shaped particles (presumably corrosion products). When these tubercles were removed and streaked on trypticase soy agar plates, *Pseudomonas aeruginosa* was the predominant organism found. Since many of the spiral and comma-shaped forms were quite dark and thick, probably because of a precipitate of metallic sulfide, it appeared that these organisms were probably *Desulfovibrio desulfuricans* or another species of *Desulfovibrio*. The organisms were treated with alkali and fluoresced red under u.v. light (365 mμ), a characteristic of these organisms as reported by Postgate (5).

This evidence suggested that sulfide may have been present in the corrosion pit since sulfate reducers are characterized by their ability to reduce sulfate, pres-

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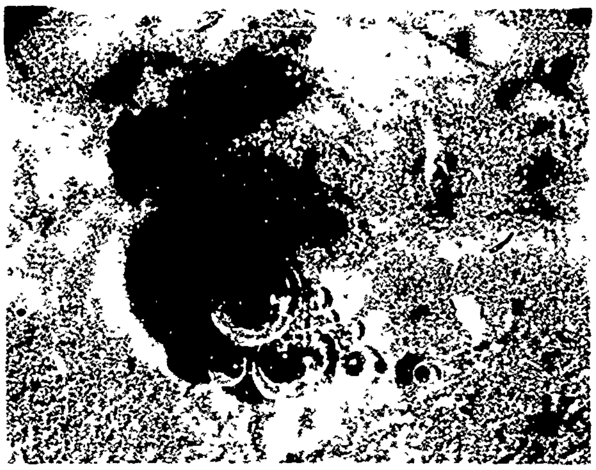

Fig. 1. Tubercle with top removed (ca. 8X mag.) showing gas evolution.

ent in the water-bottom, to hydrogen sulfide. The hydrogen sulfide might be expected to produce sulfides from the constituents of the aluminum alloy (zinc, copper, *etc.*). A simple test for the detection of sulfide is the iodine-azide reaction as described by Feigl (6). This test is based on the observation that solutions of sodium azide and iodine do not react directly, but on contact with sulfides or thiosulfates there is an immediate and vigorous evolution of nitrogen with the formation of sodium iodide

$$(2NaN_3 + I_2 \rightarrow 2NaI + 3N_2)$$

Considerable nitrogen also evolved when the iodine-azide mixture was placed in contact with the corrosion pit. This test has been repeated many times with no apparent decrease in the rate of bubbling.

Isolation of Sulfate Reducers from Pit

Several months later, a similar tank from another series of tests, this one coated with Buna-N, was found to have two large tubercles and two smaller ones.

These tubercles, however, differed from the aforementioned ones in that they were dark and did not fluoresce under u.v. light. Microscopic examination of one of the tubercles revealed a very large number of fungal filaments and yeastlike cells, Fig. 2.

This tubercle appeared to be composed primarily of fungal elements (*Cladosporium* sp.), although *Pseudomonas aeruginosa* was also present. Microscopic examination of the material in the pit revealed many

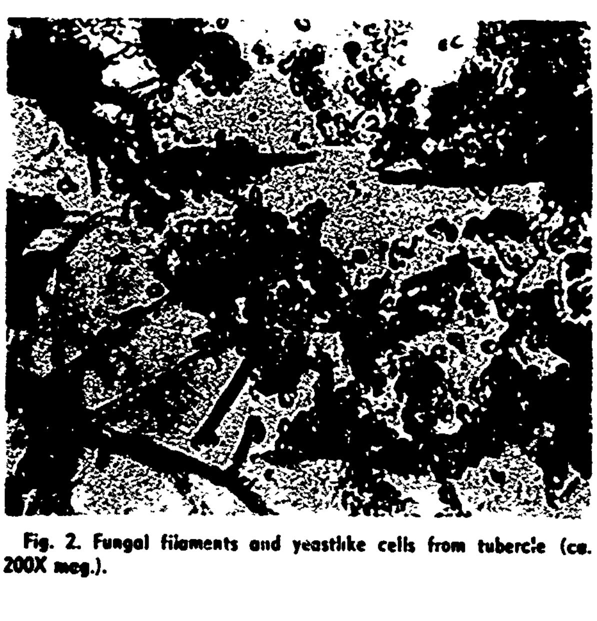

Fig. 2. Fungal filaments and yeastlike cells from tubercle (ca. 200X mag.).

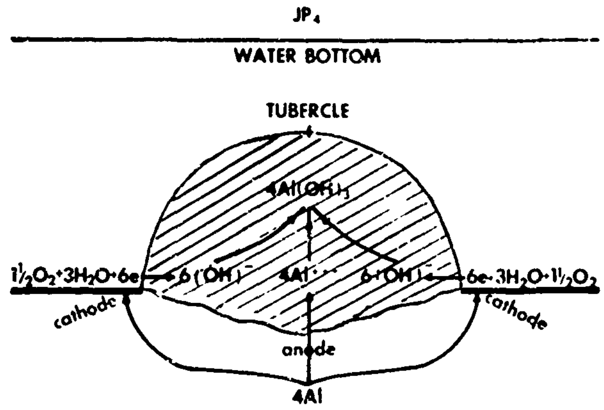

Fig. 3. Diagram of oxygen concentration cell formed by tubercle

comma-shaped organisms suggestive of the genus *Desulfovibrio*. The material in the pit was then cultured for this organism and a pure culture of *Desulfovibrio* on plates of trypticase soy broth (Difco) plus 2% agar (7) was eventually obtained.

Discussion

It appears that *Pseudomonas aeruginosa*, the fungus *Cladosporium*, and the other aerobic or facultative organisms were living in close association with the anaerobic sulfate reducer *Desulfovibrio* to form, along with the corrosion products, a visible tubercular mass on the tank bottom. Destruction of the coating by the organisms in the mass appears to have preceded pit formation.

The fungus filaments probably give a certain rigidity to the structure, anchor it more firmly to the tank bottom, and together with the other organisms provide anaerobic conditions and nutrients for the anaerobic sulfate-reducing organisms as well as possibly neutralizing toxic materials.

Such an association between heterotrophic aerobic bacteria and anaerobic sulfate reducers has been shown by Guyness and Bennett (8). They have shown that the spoilage of emulsion-cutting oils is the result of the combined activities of organisms belonging to the genus *Pseudomonas* and anaerobic sulfate-reducing bacteria. They have presented evidence that the aerobic bacteria oxidize components of the emulsion that are toxic for the sulfate-reducing bacteria, and suggest that lowering of the Redox potential and production of nutrients by the aerobic flora are secondary factors that may stimulate the growth of sulfate-reducing bacteria. A concentration cell may be established as a result of strict or highly anaerobic conditions underneath the tubercle and less anaerobic conditions at the edge of the tubercle or any exposed area of aluminum in moist contact with the tubercle, Fig. 3.

The anaerobic area under the tubercle tends to become anodic and corrode, while the area at the edge of the tubercle in contact with more oxygen tends to become cathodic. As a result of the differences in dissolved oxygen, localized corrosion may occur that may be just as marked as that when two dissimilar metals are in contact. Although the gas evolved from the tubercle was not identified, it might have been hydrogen, since there is some evidence that, when aluminum dissolves anodically, Al^{+}, as well as Al^{+++}, is formed which reduces H_2O to form Al^{+++} plus hydrogen (9).

It appears that a situation exists here similar to that of iron, where the relationship between sulfate-reducing bacteria and corrosion beneath nodules has apparently been quite well established (10), and that corrosion has been explained in terms of the oxygen concentration-cell effect. An alternative possibility is that sulfate reducers, which usually contain hydrogenase, could cathodically depolarize the aluminum according to the classical theory proposed by von Wolzogen Kühr and van der Vlugt (11). [This has been demonstrated since this paper was presented (12).] The strain isolated from the corrosion pit was found to have good hydrogenase activity.

Conclusions

In summary, sulfate reducers found in an aluminum corrosion pit suggest the presence of anaerobic conditions there which could result in an oxygen concentration-cell effect. The possibility of cathodic depolarization by the sulfate reducers must also be considered in any mechanism of aluminum corrosion.

Acknowledgments

This investigation was supported by Air Force MIPR 33-657-3RD-123, entitled "Microbial Contamination of Air Force Petroleum Products." The author thanks Robert F. Jaeger for the fluorescence microscope studies and Ralph R. Cockey for technical assistance.

This paper was presented at the Symposium on Microbiological Corrosion at the Buffalo Meeting, Oct. 10-14, 1965. Manuscript received Feb. 28, 1966; revised manuscript received July 27, 1966.

Any discussion of this paper will appear in a Discussion Section to be published in the Nov.-Dec. 1967 issue.

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