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1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE Conference Proceeding	3. DATES COVERED (From - To)
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4. TITLE AND SUBTITLE The Role of Fungi In Microbiologically Influenced Corrosion	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER 601153N

6. AUTHOR(S) Little, Brenda J. and Ray, Richard I.	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Oceanography Division Stennis Space Center, MS 39529-5004	8. PERFORMING ORGANIZATION REPORT NUMBER NRL/PP/7302-02-0006
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy St. Arlington, VA 22217-5660	10. SPONSOR/MONITOR'S ACRONYM(S) ONR
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Case histories of microbiologically influenced corrosion are presented with an emphasis on failure analysis and the techniques for diagnosing the role of fungi in the corrosion. Fungal influenced corrosion has been reported for carbon steel and aluminum fuel tanks; carbon steel cables; and painted and unpainted ship holds containing wet and dry cargos. Deterioration of fiber-reinforced composites and glass has also been attributed to fungal species.

15. SUBJECT TERMS
fiber-reinforced composites, fungi, influenced corrosion

20030523 141

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON Brenda Little
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (228) 688-5494

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The Role of Fungi in Microbiologically Influenced Corrosion

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Abstract

Case histories of microbiologically influenced corrosion are presented with an emphasis on failure analysis and the techniques for diagnosing the role of fungi in the corrosion. Fungal influenced corrosion has been reported for carbon steel and aluminum fuel tanks; carbon steel cables; and painted and unpainted ship holds containing wet and dry cargos. Deterioration of fiber-reinforced composites and glass has also been attributed to fungal species.

Introduction

The term microbiologically influenced corrosion (MIC) is used to designate corrosion due to the presence and activities of microorganisms. Microorganisms can accelerate rates of partial reactions in corrosion processes and/or shift the mechanism for corrosion.¹ Most laboratory and field MIC studies have focused on bacterial involvement; however other single-celled organisms, including fungi, can influence corrosion. Fungi dominate the microflora in humid atmospheres, including fuel/water interfaces and in soil. For example, Geesey² stressed the potential corrosion problem for metal containers selected for storage of nuclear waste in terrestrial environments.

Liquid water is needed for all forms of life and availability of water influences the distribution and growth of microorganisms. Water availability can be expressed as water activity (a_w) with values ranging from 0 to 1.0. Microbial growth has been documented over a range of water activities from 0.60 to 0.998. Fungi are the most desiccant-resistant microorganisms and can remain active down to $a_w = 0.60$ whereas few bacteria remain active at a_w values below 0.9.³ The temperature range in which living organisms can grow is that in which liquid water can exist, approximately 273-373 °K. Life is possible over concentrations of H^+ ions varying by several orders of magnitude, and some individual microorganisms can grow over a range of 10 pH units or more. Many microorganisms can withstand hundred-fold or greater variations in pressure. The highest pressure possible in the depths of the sea is only mildly inhibitory to growth of many microorganisms. Heavy metal concentrations as low as 10^{-8} M can inhibit growth of some microorganisms, while others may be resistant to concentrations of a million-fold greater. Microbial species show thousand-fold differences in susceptibility to irradiation.²

Most fungi are aerobes and are only found in aerobic habitats. Fungi are nonphotosynthetic organisms, having a vegetative structure known as a hyphae, the outgrowth of a single microscopic reproductive cell or spore. A mass of threadlike hyphae make up a mycelium.³ Mycelia are capable of almost indefinite growth in the presence of adequate moisture and nutrients so that fungi often reach macroscopic dimensions. Spores, the non-vegetative dormant stage, can survive long periods of unfavorable growth conditions, e.g., drought and

starvation. When conditions for growth are favorable, spores germinate. Fungi are ubiquitous in atmospheric and aquatic environments where they assimilate organic material and produce organic acids including oxalic, lactic, formic, acetic and citric. The following is a review of fungal influenced corrosion, emphasizing the environmental conditions contributing to the proliferation of fungi and mechanisms for the resulting corrosion.

Metals exposed to hydrocarbon fuels

Fungal contamination and decomposition of hydrocarbons are well-documented phenomena.⁴⁻²⁰ The major limitation for microbial activity in fuels is the presence of water.⁹ An important characteristic of oils related to microbial interaction is limited water solubility and concentration of microbial growth at oil/water interfaces. The volume of water required for microbial growth in hydrocarbon fuels is extremely small. Since water is a product of the microbial mineralization of organic substrates, it is possible for microbial mineralization of fuel to generate a water phase for further proliferation. For example, *Cladosporium resinae*, the kerosene fungus, grew in 80 mg water per liter of kerosene and after four weeks incubation, the concentration of water increased more than ten-fold.⁶

The first step in microbial decomposition of hydrocarbons is an aerobic process that requires molecular oxygen. Anaerobic degradation of hydrocarbons by microorganisms proceeds at negligible rates.⁴ Walker *et al.*²⁰ compared degradation of hydrocarbons by bacteria and fungi. Bacteria showed decreasing abilities to degrade alkanes with increasing chain length. Filamentous fungi did not exhibit a preference for specific chain lengths.

The first products of microbial oxidation of hydrocarbons are alcohols, aldehydes and aliphatic acids. Formation of hydroxy acids has also been reported.⁶ Several authors have reported a decrease in bulk pH due to metabolites produced during growth of fungi.^{16,17} De Mele¹³ demonstrated a correlation between growth of *Cladosporium* and pH at fuel/water interfaces and measured pH values between 4.0 and 5.0 in the bulk medium. Weissman and Drewello²¹ reported both strongly acidic conditions and alkaline conditions due the growth of *Apergillus niger* and *Penicillium* sp in a glucose-containing medium. Decreasing pH was attributed to accumulation of organic acids out of the tricarboxylic acid cycle and glycolysis. The concentration and spectrum of acids changed during the experiment due to continuous biogenic degradation of gluconate and accumulation of unoxidized metabolites. Cell death or lysis may contribute to higher pH, but does necessarily mean a cessation or reduction in the rate of corrosion.

Fungal influenced corrosion has been reported for carbon steel and aluminum alloys exposed to hydrocarbon fuels during transport or storage. The following mechanisms for MIC in fuel/water systems were elucidated by Videla *et al.*¹⁰: 1) local increase in proton concentration derived from organic acidic metabolites, 2) increase of the oxidizing characteristics of the medium favoring pitting attack, 3) metabolite production decreasing the surface energy of the interface passive film/electrolyte, 4) microbial adhesion enhancing metal dissolution and 5) microbial uptake of fuel additives, including corrosion inhibitors. Rosales¹⁸ demonstrated metal ion binding by fungal mycelia, resulting in metal ion concentration cells on aluminum surfaces. Differential aeration caused by the adherence of fungal mats can cause crevice corrosion.¹² De Mele¹³ reported that corrosivity increased with contact time due to accumulation of metabolites under microbial colonies attached to metal surfaces. De Meybaum and de Schiapparelli¹⁴ demonstrated that the metabolic products

enhanced aqueous phase aggressiveness even after the life cycle of *Cladosporium* sp. was completed.

The corrosion rate of carbon steel in fresh waters is independent of pH between 4.5 and 9.5.²² This has been confirmed in tap water and distilled water. Over this range of pH values corrosion is controlled by oxygen diffusion. At pH 4.0 or below hydrogen evolution takes place and corrosion increases rapidly. It is well established that bulk pH cannot be used to predict pH under microbial colonies. Furthermore as acid is consumed in a corrosion reaction, it does not contribute to bulk pH. Within the passive pH range, 4 to 9, aluminum alloys resist corrosion in solutions of inorganic chemicals but are subject to pitting in aerated solutions containing halides.

Polymer-coated metals

Numerous reports document fungal degradation of coatings and in some cases corrosion of the underlying metal.²³⁻²⁵ Stranger-Johannessen²⁶ reported that ship cargo holds coated with chlorinated rubber and carrying dry cereals and woods were severely corroded within months. Heavy pitting and reduced thickness of the steel plate were observed. Corrosion products were populated with viable fungi. Stranger-Johannessen demonstrated that the fungi derived nutrients from degradation of the protective coating in addition to the cargo. Corrosion resulted from acidic metabolic by-products. Stranger-Johannessen²⁷ reported deterioration of the epoxy resin coating of ship holds filled with molasses, fatty oils and other fluid cargoes. She also confirmed fungal degradation of polyurethane cable sheathing in the marine environment.²⁸

Lavoie and Little²⁹ isolated the following fungal genera from polyurethane-coated 2024 aluminum helicopter interiors: *Pestotia*, *Trichoderma*, *Epicoccum*, *Phoma*, *Stemphylium*, *Hormodendrum* (also known as *Cladosporium*), *Penicillium*, and *Aureobasidium* (2). Several of the genera, including *Aureobasidium* penetrated the polyurethane topcoat, but not the chromate primer. The result was disbonding of the topcoat (Figure 1a & b), but there was no corrosion of the base metal as long as the primer was intact. Stranger-Johannessen documented the biocidal properties of zinc chromate primer.³⁰ None of the isolates could use the polyurethane coating as a sole source of nutrients; however, all grew on hydraulic fluid accumulated on painted interior surfaces during routine operations. Glossy finish polyurethane was colonized more rapidly than the same formulation with a flat finish. Aged paint fouled more rapidly than new coatings. Laboratory tests demonstrated that in the presence of hydraulic fluid, all of the isolates caused localized corrosion of bare 2024 aluminum.

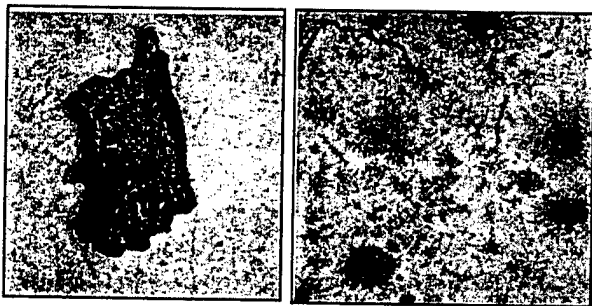


Figure 1 – Penetration of polyurethane paint by fungi, causing disbonding. a) (left) Topside of polyurethane paint chip b) underside of the same paint chip.

Metals coated with greases

Seven-strand carbon steel cable is used as wire rope and as tendon in post-tension construction. Each cable is made of six strands wrapped around a central core. When cable is used as rope or highline, the cable is coated with thick maintenance grease and threaded onto wooden spools (Figure 2 a-c), wrapped in brown paper and black plastic. The maintenance grease is applied to the cable to provide corrosion protection. Wire rope is stored on wooden spools for weeks to months before being used. In an investigation of localized corrosion on wire rope stored on wooden spools, fungal growth was observed on interiors of some wooden spools stored outdoors.³¹ Corrosion was most severe on wraps of wire in direct contact with the wooden spool flanges. *Aspergillus niger* and *Penicillium* sp. were isolated from wooden spool flanges. Isolates could not grow on the protective grease as the sole nutrient source. The isolates grew on wood and produced copious acids and CO₂. In all cases localized corrosion was observed in areas where acidic condensate (pH 4.9) dissolved the maintenance grease.

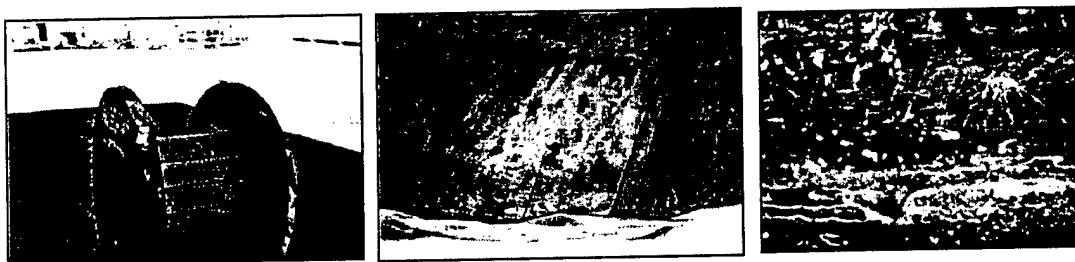


Figure 2 – (from left) a) wooden spool on which wire rope was stored. pieces of paper are attached to rim edges. b) inside surface of wooden spool. white deposits are the result of fungal growth. c) light microscope photograph showing fungal mycelia attached directly to wire and associated with localized corrosion, 40x.

Carbon steel cables used as tendons are typically lubricated with hydrocarbon grease before insertion into preplaced polyvinyl chloride ducts in concrete slabs (Figure 3a). Polyvinyl chloride ducts provide corrosion protection and the grease facilitates insertion of the cable into the duct. Cables are post-tensioned from one or both ends after the concrete has achieved sufficient strength and anchor plates are attached. Water can be introduced during construction, or can accumulate after construction. Little *et al.*³² isolated *Fusarium* sp., *Penicillium* sp. and *Hormoconis* sp. from corroding tendons in a post-tensioned structure. The pH of the water associated with the corrosion products was consistently 2 or below. The isolates were used to inoculate tendons in sheathes (Figure 3b). In laboratory experiments, Little *et al.* demonstrated grease degradation and concomitant acid production using Fourier transform infrared spectroscopy (FTIR). FTIR results are displayed as absorbance (y-axis). The fingerprint region of the infrared spectrum for a reference metal soap grease is given in Figure 4. Bands 1460, 1377 and 722 wavenumbers indicate deformation vibration modes for long chain hydrocarbons. Absorption bands at 1580 and 1560 wavenumbers relate to stretching modes of the carboxylate anion in association with a metal ion such as calcium or lithium. The most notable features of spectra for fungi reference spectra were amide I and II stretching frequencies at 1650 and 1590 wavenumbers (Figure 5). Under the experimental conditions, these absorption bands indicate the presence of proteins and are indicative of fungi. The association of fungi with corrosion products and the details of the corrosion were documented with scanning electron microscopy. Localized corrosion was observed for all inoculated tendons (Figures 6a & b). In all cases, shallow craters were located under

corrosion products. Cracking in association with the craters was observed on two wires from a single tendon. Petri dishes inoculated with grease from the corroded areas were positive for *Fusarium* and *Hormoconis*. There were no indications of chloride in EDS spectra of the grease. Four FTIR spectra collected from a single fungal contaminated tendon demonstrated varying degrees of degradation. Spectra are arranged in order of increasing degradation (Figure 7a-d). The broad peak at 3300-3200 wavenumbers is indicative of bonded hydroxyl groups, such as those found in hydroxy acids. Peaks immediately below 3000 wavenumbers (2924 – 2850) are typical of hydrocarbons and are due to methyl and methylene groups. The peak for bonded -OH in carboxylic acids is in the same region. Peaks at 1000 wavenumbers are due to the presence of -C-O-C- bonding, a further indication of oxidation. As the grease is oxidized, the carboxylate contribution (1560 wavenumbers) decreases and the carbonyl contribution (1750 wavenumbers) increases. In 7a there is a strong carboxylate with an absence of carbonyl. In 7b the carbonyl contribution has increased and the carboxylate decreased. Peaks at 3200 and 1000 wavenumbers have increased. The effect is more pronounced in 7c. In all cases amide peaks are prominent. In 7d the spectrum indicates the presence of a light oil. The carboxylate is missing and the carbonyl is prominent.

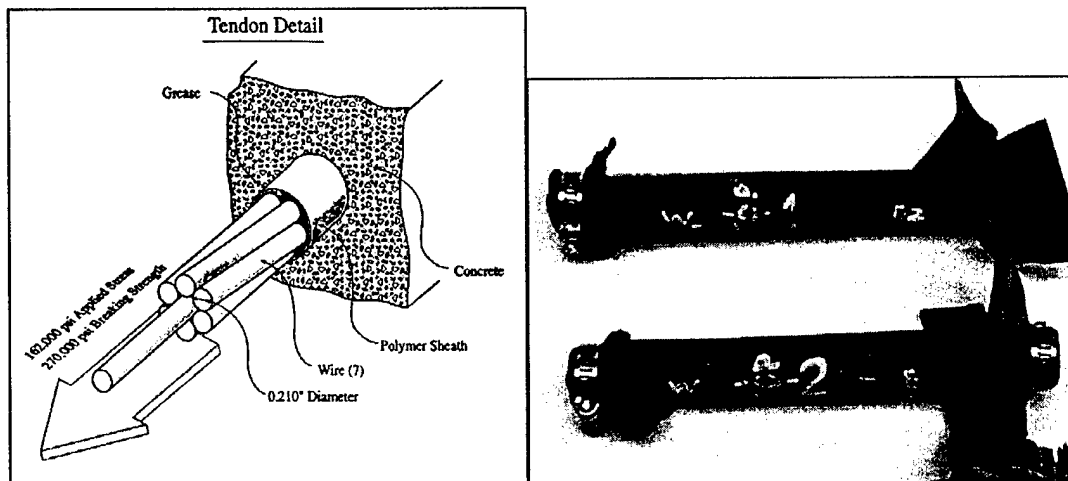


Figure 3. – a) (left) Details of the tendon in the sheath; b) Sheathed tendons after inoculation.

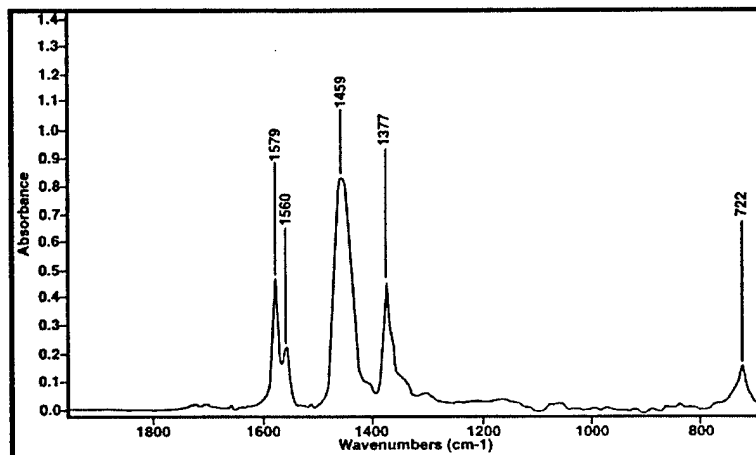


Figure 4. – Reference spectrum for metal soap grease.

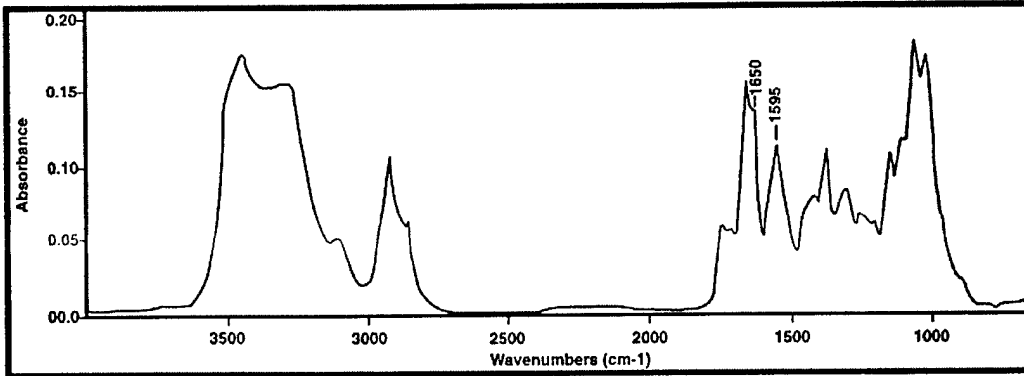


Figure 5. – Reference spectra for *Fusarium*.

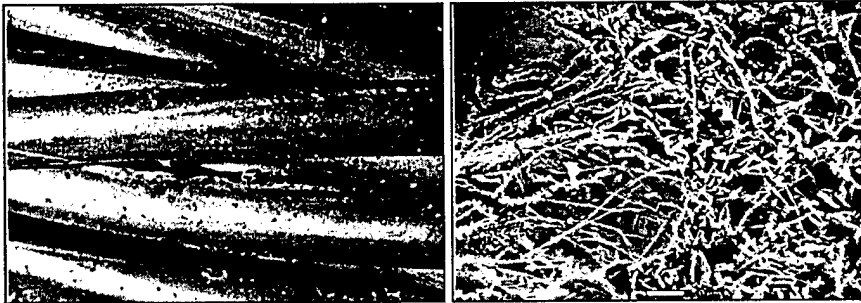


Figure 6. – a) (left) Fungi and corrosion products on inoculated tendon 6X. b) ESEM micrograph of fungi and corrosion products.

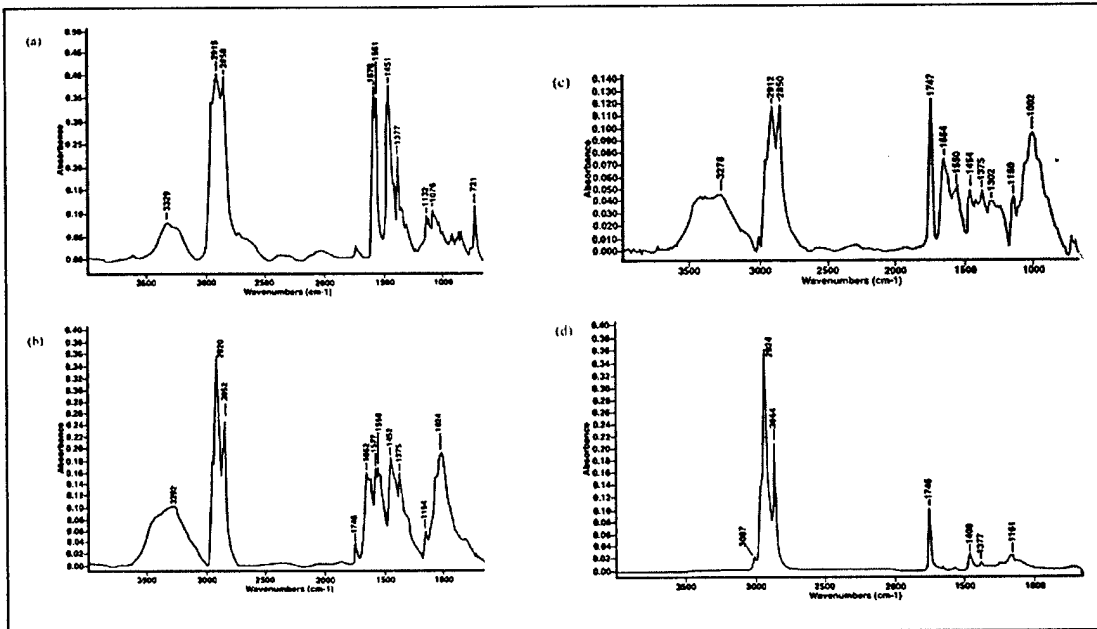


Figure 7. – Spectra collected from a single inoculated tendon. a) Grease and corrosion products, b) Grease and corrosion products, c) Grease and corrosion products, d) Oily residue.

Toropova *et al.*³³ determined that 80% of lubricants used for protecting materials were contaminated with 37 biological agents (21 fungi and 17 bacteria) during storage and use, independent of climate or relative humidity. They identified the following species were most frequently encountered in lubricating oils: *Aspergillus versicolor*, *Penicillium chrysogenum*, *Penicillium verrucosum*, *Scopulariopsis brevicaulis*, *Bacillus subtilis* and *Bacillus pumilis*. Organisms isolated from one particular lubricant could not always grow vigorously on others. Microbial growth in lubricants was accompanied by changes in color, turbidity, acid number and viscosity. Acid number refers to the acid or base composition of lubricating oils and is also referred to as corrosion number.

Non-metallics

Biodeterioration due to fungi has been documented for the following non-metallic materials: cellulose (paper, composition board and wood); photographic film; polyvinyl chloride films; sonar diaphragm coatings; map coatings; paints; textiles (cotton and wool); vinyl jackets; leather shoes; feathers and down; natural and synthetic rubber; optical instruments; mechanical, electronic and electric equipment (radar, radio, flight instruments, wire strain gages, helicopter rotors); hammocks; tape; thermal insulation; brick masonry, marble, sandstone and concrete; and museum valuables and glass. Gu *et al.*³⁴ investigated biodeterioration of fiber reinforced composites and carbon fibers used in composite materials. They concluded that fungi were responsible for an observed decrease in electrochemical properties. Deterioration of physical properties was not measured. Kaiser *et al.*³⁵ investigated fungal growth on medieval glass paintings. They reported that fungi can assimilate ions derived from glass substrata. Excretion of organic acids and enzymes causes corrosion of stones. Ammonia, calcium, magnesium, potassium, sodium, phosphate and iron were leached from minerals. Di- and trivalent cations were chelated with organic acids,

Summary

Fungi can influence corrosion via numerous mechanisms including the following: 1) local acid production under colonies, 2) reduction of bulk pH in a liquid medium, 3) direct degradation of coatings, 4) dissolution of protective greases, 5) under deposit corrosion and 6) metal concentration cells. Fungi proliferate in humid environments and can assimilate low molecular weight molecules and elements from surfaces.

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