Applications of a Morpholine-Derivative Product in Fuel Preservation

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SUMMARY

Microbial contamination and subsequent fuel-quality deterioration has been a problem for many years, and continues in that regard today. Bacteria, and especially fungi, can create filter-blocking and injector-fouling sludge and deposits, damage storage-tank interior walls, and impair fuel quality. Biocides used to prevent such events, in addition to being effective in controlling such microorganisms, must not do any harm to the fuel-storage system, the fuel itself, or the engines which use such fuel. Nitrobutylmorpholine is one such chemical—it has a broad spectrum of antimicrobial activity, a useful solubility profile, and contains no potentially harmful atoms. Performance testing, detailed below, shows it to offer benefits in preservation of fuels against microbial proliferation without detrimental impact.

MICROORGANISMS AND HYDROCARBON FUELS

Microbial contamination of hydrocarbon fuels, leading to consequent deterioration of fuel performance, has been recognized for many years [1]. Fungi, living at a fuel/water interface in a storage tank, can proliferate by using the hydrocarbon as an energy source. As biomass (slime) accumulates through microbial aggregation, it can also trap other particulates, and semi-solid matter from the interface can sink to the bottom of the tank as sludge, or adhere to the tank walls as biofilm. Moreover, production of surface-active microbial-metabolism products at the interface can create emulsions there. Fungi, such as *Hormoconis (Cladosporium) resinae, Candida albicans* and *Aspergillus niger* are the most problematic type of fuel-contaminating microorganisms. However, bacteria, including anaerobic sulfate-reducing bacteria (SRB) such as *Desulfovibrio desulfuricans* and a considerable variety of heterotrophic bacteria, can proliferate, especially beneath biofilms or sludge layers, and corrosively damage fuel-storage tank interiors. Further, bacterial slime, as well as that of fungal origin, is documented as being detrimental in fuel systems, with *Pseudomonas* spp. as a common source [2].

Microbially-contaminated fuel will, in turn, contaminate systems downstream in the fuel-use-chain, and a higher rate of fuel turnover in a storage system, especially when associated with multiple fuel sources, can result in a greater possibility for contamination. While contamination of diesel fuel, both marine and highway, is best-documented, aviation fuel and gasoline are also susceptible to microbial growth, as are certain turbine, crankcase and hydraulic oils, and even stored crude oil. In fact, recent changes in gasoline-additive regulations have created systems more prone to contamination than previous ones. Aviation fuels which contain significant levels of the anti-icing additive ethylene glycol monomethyl ether (EGME) are less liable to permit microbial survival than are deicer-free systems [3]. However, due to its unfavorable toxicological profile, the use of EGME was discontinued in the mid-1990's. Its legacy additive, diethylene glycol monomethyl ether (DiEGME) does not share its antimicrobial performance characteristics.

The most-obvious detrimental effects of contaminated fuel are tank and transfer-line fouling, and blinding or plugging of fuel filters and injector nozzles, due to the action of sludge. The tighter tolerances of electronically-controlled fuel systems render them easier to foul and more expensive to replace. Additionally, SRB, as well as other facultative and obligately anaerobic bacteria, thrive in the oxygen-deficient areas beneath biofilms, producing hydrogen sulfide and weak organic-acid by-products which react with bottom-water chlorides, sulfates and nitrates to form inorganic acids, corrosive to metal tanks (microbially-influenced corrosion - MIC - of tank surfaces). Hydrogen sulfide is extremely toxic and is responsible for the "rotten-egg" odor in heavily-contaminated fuels. Moreover, the creation of oxygen-deficient regions in the tank contents causes oxygen gradients, which have the potential to induce galvanic pitting corrosion. In some cases, microbes may be able to attack carbon- or glass-fiber reinforced polymeric composite (e.g. fiberglass) tank linings by using the resins as food sources. Microbially-induced emulsions of water in hydrocarbon fuels can adversely affect combustion properties, and direct microbial attack on hydrocarbons themselves can result in fuel-chemistry changes. Further, additives in fuels are sometimes special targets for microbial action [4].

Rigorously water-free fuel systems will be hostile to microbial proliferation, since microorganisms need water to grow. It is very important to employ good "housekeeping" practices in order to prevent water build-up in fuel-storage tanks. However, temperature variations (such as warm days and cool nights) can cause condensation of the atmospheric water vapor in storage-tank headspaces. Additionally, contamination by rainwater entry, or the use of water-displaced tankage, will provide sufficient water to encourage microbial growth and contamination. Tank-design considerations can assist in fuel-quality maintenance through the installation of conical bottoms on storage tanks for more-efficient water drainage, and filters on air inlets of tank vents to reduce introduction of airborne particulates. While settling within fuel-storage tanks can assist in sludge removal, filtration is more time-efficient, since settling out may require up to one week of undisturbed storage [5]. It should be noted, though, that filtration will not remove free-floating single-cell microbes from the fuel, nor will it remove microbes growing within biofilms on system surfaces. Other maintenance measures besides water exclusion and sludge removal include tank-contents microbial-load monitoring, especially sampling from fuel-water interfaces and infrequently-drained locations. However, viable, free-floating microbes will so detected only if the fluid has been agitated prior to sampling. Moreover, an acidic pH shown by a water-bottom sample can indicate corrosive conditions in the tank bottom. It follows, then that an effective fuel monitoring program will include measurement of fuel filterability, presence of water, presence of sediment or particulates, and presence of microbes. The final step in an effective fuel-maintenance program is proper utilization of an effective antimicrobial agent.

DESIRED FUEL-BIOCIDE ATTRIBUTES

In order to offer value in protecting hydrocarbon fuels against microbial deterioration, there are several behaviors which a biocidal product must exhibit [6]. Among its most important features, it should not have any deleterious effect on any of the engine parts nor on the engine's performance. It should not cause corrosion or pitting of metals, including steel, aluminum, magnesium and various alloys thereof. The biocide should not degrade the combustion properties of a fuel which contains it.

Other properties desired in a fuel biocide include not producing ash upon combustion, and not creating deposits in, nor harmful emissions from, combusted fuel containing it. A fuel biocide should be sufficiently soluble in fuel and/or water (preferably both) to function against microbial growth in the target phase and at the phase interface. It should not be surface-active enough to cause emulsions of fuel and water, and it should remain chemically and physically stable over the temperature ranges which it is expected to encounter during storage. Finally, it should remain, in suitable concentrations, in the desired fuel-system phase for a period of time sufficient to destroy or prevent microbial growth, neither evaporating from the liquid nor forming a separate phase upon standing.

In addition to the above properties, the product should be microbially active at economical concentrations. The two basic modes of antimicrobial use of such a product are to add it in slug-dose fashion to an already-contaminated fuel system in order to quickly stop further bacterial and fungal growth, or to employ it at lower, maintenance levels in uncontaminated or just-cleaned-up systems, to prevent any microbes from starting to multiply therein.

NITROBUTYLMORPHOLINE-PRODUCT PROPERTIES

Chemically, the nitrobutylmorpholine product (NMEND) is the Mannich-reaction product created from morpholine, formaldehyde and 1-nitropropane; as supplied, it is an 80%-active anhydrous liquid material. It should be noted that NMEND is composed only of carbon, hydrogen, nitrogen and oxygen—it contains no boron, halogen or sulfur atoms. NMEND is completely fuel-soluble, and water-soluble up to about 1%. Its partition coefficient has been determined to be about 0.26 [7]. This solubility behavior suggests that the most effective way to utilize NMEND as a stored-fuel preservative would be to inject an appropriate amount of it into a fuel-storage tank through the bottom drain valve, permitting it to saturate the water bottom and permeate upward through the fuel-water interface into the lower portion of the fuel layer.

NMEND is a slightly-to-moderately alkaline product, whose saturated aqueous solution has a pH of about 9. Due to its amine functionality, it can be expected to neutralize acidic microbial by-products, and thus aid in corrosion protection. Further, the product as supplied has a flash point (PMCC) of about 79°C, a freezing point of about 10°C and a vapor pressure at 20°C of about 13 mm Hg (1.73 kPa).

The microbiological spectrum of NMEND extends to both bacteria and fungi (as well as to algae, which are not a factor in fuel contamination), including several of the most common ones recovered from contaminated fuel. In laboratory tests of its minimum inhibitory concentration against single strains, the NMEND product was shown to be effective at 50-100 ppm vs. *Desulfovibrio desulfuricans,* at 100-200 ppm vs. *Candida albicans,* at 400-500 ppm vs. both *Aspergillus niger* and *Pseudomonas aeruginosa*, and at 600-700 ppm vs. *Hormoconis resinae*. [8].

With regard to regulatory compliance, 4-(2-nitrobutyl)-morpholine has a CAS Registry No. of 2224-44-4, and an EINECS No. of 218-748-3. The NMEND product has a U.S. EPA Registration No. of 464-659, and is registered there for antimicrobial use in metalworking fluids and in die-cast lubricants and mold-release agents, as well as in fuel and hydrocarbon preservation. In Europe, it has been notified under the Biocidal Products Directive by the manufacturer.

NITROBUTYLMORPHOLINE-PRODUCT PERFORMANCE TESTING

Microbiology

Both speed of kill (in already-contaminated systems) and persistence of effect (to maintain acceptably-low microbial levels) are important in a fuel biocide. NMEND was tested in model systems of No. 2 diesel fuel stored over ordinary tap water or synthetic seawater (simulating seawater ballasting aboard ship), containing approximately 10^6 CFU/mL bacteria (*Desulfovibrio desulfuricans* and *Pseudomonas aeruginosa)* and 10^4 CFU/mL fungi (*Hormoconis resinae* and *Candida tropicalis*) [9]. The antimicrobial-testing protocol used was that described in ASTM E1259-88. In the fresh-water phases, 125 ppm (v/v) of NMEND reduced nearly all the microbial populations by more than 80% in less than one hour (*Hormoconis resinae* was reduced by approximately 50% under these conditions) and all were reduced to less than 90% after 24 hours. At 250 ppm of NMEND, populations of all the species were reduced to less than 1 CFU (Colony-Forming Units)/mL, described as Below Detectable Limits (BDL), within 8 hours. In the salt-water phases, 250 ppm of NMEND reduced all species except *Hormoconis resinae* to BDL within 8 hours; this fungus was reduced by 90% under the test conditions. In the fuel phases of the tested systems, 125 ppm of NMEND reduced all populations to BDL within 4 hours.

In persistence-of-effect testing in the above systems, both 125 and 250 ppm of NMEND maintained microbial populations at BDL for the entire 12-week test period in the fresh-water bottoms, while 250 ppm NMEND maintained the sea-water populations at BDL for 12 weeks. The untreated water-phase controls remained at about 7.5×10^7 CFU/ mL total population during the 12-week test period.

In another test series, NMEND and methylene-*bis*-thiocyanate (MBT) were tested in a system of regular, unleaded gasoline over synthetic water [10]. The gasoline contained approximately 12% *t*-alkyl methyl ethers as oxygenated additives, and the systems were inoculated with uncharacterized mixed microbial populations isolated from actual spoiled fuels. After a test interval of 7 months, 300 and 1,000 ppm of NMEND, and 40 ppm of active MBT, showed significant inhibition of total microbial population in the water phase, as measured by catalase activity. Only 1,000 ppm of NMEND showed significant control of acid-producing bacteria after 7 months, while all treatments had reduced anaerobic bacteria significantly compared to the water-phase controls after 7 months.

In the fuel phase after 7 months, catalase-activity testing showed that 1,000 ppm of NMEND had provided more than 90% total-population inhibition, while 300 ppm NMEND and 40 ppm active MBT gave greater than 75% inhibition after 7 months. (It should be noted that only 1,000 ppm NMEND maintained a total population reduction of greater than 90% as measured by catalase activity in both the water phase and the fuel phase.) In the fuel phase after 7 months, 1,000 ppm of NMEND was again the most-persistent treatment against acid-producing bacteria, while 300 ppm and 1,000 ppm NMEND, as well as 40 ppm active MBT, effectively inhibited anaerobic, sulfate-reducing bacteria.

Fuel Effects

In addition to providing effective microbial control, a fuel biocide must not cause any adverse effects. Static-load tests in a Mercedes 350 diesel engine, coupled to a General Electric dynamometer capable of absorbing 200 horsepower (2.14×10^3 Kg-cal/min), showed that diesel fuel containing as much as 1,000 ppm (v/v) of NMEND had no adverse effect at all on either specific fuel consumption or NO emissions [11]. The engine loads in this test series ranged up to 120 hp. Although not fully approved for use in aviation fuel, 1,000 ppm of NMEND has been documented in the same study to have no adverse effect on aviation-fuel properties, or corrosive effects on gas-turbine components, when tested using appropriate ASTM procedures.

In comparative stored-gasoline chemistry testing after a 7-month test period, both NMEND and MBT maintained fuel filterability, as opposed to the contaminated, untreated control [12]. 1,000 ppm NMEND inhibited the microbially-induced loss of C_5 and C_6 species by 40%, while 40 ppm MBT provided a 20% inhibition. NMEND inhibited microbially-caused loss of oxygenated additives (*t*-alkyl methyl ethers) by 73%, compared to 50% loss-inhibition by MBT. Moreover, the NMEND inhibited losses in *n*-paraffins, and accompanying increases in alky*l iso*-paraffins and aromatic-compound concentrations, to a greater extent than did the MBT (NMEND gave 62% inhibition of alkyl *iso*-paraffins increase and 41% inhibition of aromatics increase, compared to 25% and 14% respectively, for MBT.) Finally, only NMEND contributed significantly to maintaining bottom-water alkalinity over the 7-month test period.

CONCLUSION

In this presentation, the authors have described the detrimental effects which can be caused by unchecked microbial growth in hydrocarbon fuels, and efforts which should be undertaken to preclude such proliferation through proper maintenance and monitoring. Such a program will include appropriate use of a suitable antimicrobial agent, whose desired attributes are herein documented. One material which meets the criteria is NMEND; its chemical and antimicrobial properties are detailed, as is its performance testing in fuel-storage systems. NMEND provides the desired antimicrobial effects of both quick-acting shock effect and long-term preservation against undesirable growth, without producing detrimental effects in either fuel combustion or engines utilizing such preserved fuel.

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