LL #66

Ferreting Out the Identity of Gasoline Additives

by Jim Weaver and David Spidle

Chemical dispersing agents for oil spills, hydraulic fracturing fluids for natural-gas production, and chemicals serving as gasoline additives share a common characteristic—for the most part, they are proprietary compounds. In the name of competitive advantage, companies carefully guard the chemical recipes of these products and are allowed by the federal government to claim "confidential business information" (CBI) status for them. As a consequence, there could be additives in released fuels that cause future heartburn for the L.U.S.T. program. The word "could" must be emphasized because, for a compound to cause a problem, it would have to be present in sufficient concentration in the fuel, have high enough water solubility to enter an aquifer, have low enough degradation to persist, and be toxic at the concentration where a receptor would encounter it. Although these criteria present a high bar to pass, we can look to the lead scavenger ethylene dibromide (EDB) as a past example of an additive that is indeed a continuing problem (see L.U.S.T.Line #47).

The complexity of additives can be seen in USEPA's additive registration form, which lists 50 purposes for gasoline additives (http://www.epa.gov/oms/regs/fuels/forms/3520-13.pdf). These include detergents, anti-oxidants, metal deactivators, corrosion inhibitors, and anti-icing agents, among many others. The concentrations of these additives in gasolines can range from low parts per million (ppm) to low percent levels. For comparison, benzene in reformulated gasoline is currently limited to less than 1 percent or 7,500 ppm; much higher than the majority of additives. The chemical classes of additives include petroleum fractions, low molecular weight alcohols, complex binders, organometallic compounds, surfactants, and polymers (VFJ, 2006). "Classic" additives, as defined by VFJ are those with known chemical, toxicological, and environmental risk properties. These tend to be compounds that have been used in gasolines over a long period of time, while newer compounds tend to be surfactants, polymers, and organometallics (VFJ, 2006).

Chemical Analysis

Some additives have been identified in fuel handbooks, automotive industry conference proceedings, and journal papers, but many are publicly unknown. Lack of chemical identification coupled with the variety and complexity of these compounds, makes chemical analysis a daunting task. Despite the difficulties, two approaches have been tried.

The first approach is to equilibrate gasoline with water and analyze the extracts by liquid chromatography/mass spectroscopy. This was done for a set of Swiss gasolines by Torsten Schmidt and colleagues at the Swiss Federal Institute of Technology in Zurich (Schmidt et al., 2002). The work resulted in a list of 17 polar compounds that have a high tendency to partition to groundwater Estimation of the partitioning behavior of these compounds led to an approximate approach for estimating their concentrations in groundwater. The results showed that many of these chemicals have high water solubility and would be released from their source gasolines relatively rapidly. Thus, they may not persist in the gasoline itself. In a roughly

similar hunt for compounds, Weaver et al. (2009) analyzed fuel-grade ethanol and looked for impurities. A number of higher molecular-weight alcohols were found and are listed in Table 1, along with Schmidt's set of compounds and a number of additives identified in other literature. Notably for both of these projects, the focus was on identifying constituents, but not their toxicity.

A second approach looks from the top down. In Denmark, five major petroleum companies revealed the identity of additives they were using to a consulting firm, which agreed to keep the identities of the compounds confidential unless a simplified screening determined that they might cause ill effects (VFJ, 2006). The companies identified around 100 compounds and of these, eight were identified as potentially harmful. These compounds are listed in Table 1 alongside the chemicals identified from the "bottom up."

Questions from LUSTland

In the United States, all gasoline and diesel motor-vehicle fuel additives are required to be registered in accordance with the regulations in 40 CFR 79. USEPA requires that the producer provide information on the chemical composition and methods of analysis for determining the presence of each compound and impurities. The manufacturer is also asked to submit any information it has on "the effects of this fuel additive on all emissions; the toxicity and any other public health or welfare effects of the emission products of this fuel additive." In a few cases, USEPA has required that these fuels and fuel additives be tested for possible health effects, notably ethanol, ethers, MMT and cerium-based additives for diesel fuel. The manufacturer can assert that the product information is CBI, and, presumably, many do. So although USEPA holds composition information on registered additives, CBI information cannot be disclosed to the public, including LUST program managers, and besides that, the health-effects from ingestion of water are likely to be unknown unless well-studied chemicals are involved.

USEPA and/or outside groups have questioned the need for CBI claims for oil spill dispersants, hydrofracking fluids, and chemicals in commerce (Hogue, 2010). These increased concerns might indicate a future move toward more disclosure of proprietary chemicals. In the meantime, research is needed on possible impacts of additives on ground water at L.U.S.T. sites. We suggest a program of research on these chemicals which would begin to identify additives in US gasolines. Publicly-identified additives as in Table, 1 form a starting point for a study of impacts to ground water. If these chemicals are found, then attention can be focused on their health effects. Both of these factors -- the exposure and the effects -- need to figure into decisions concerning site management and we are only at the beginning stage of investigating these chemicals.

Disclaimers

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for publication.

Table 1. Some publicly identified gasoline additives.

Class	Chemical	CAS No	Note	Source
Aromatic Amines	aniline	62-53-3	Water equilibrated with gasoline	Schmidt et al., 2002
	p-toluidine	106-49-0	Water equilibrated with gasoline	Schmidt et al., 2002
	o-toluidine	95-53-4	Water equilibrated with gasoline	Schmidt et al., 2002
	3,4-dimethylaniline	95-64-7	Water equilibrated with gasoline	Schmidt et al., 2002
	2,6-dimethylanaline	87-62-7	Water equilibrated with gasoline	Schmidt et al., 2002
Aliphatic Amines	diethanolamine	111-42-2	Potential environmental impact	VFJ, 2006
	triethanolamine	102-71-6	Potential environmental impact	VFJ, 2006
Phenols	phenol	108-95-2	Water equilibrated with gasoline	Schmidt et al., 2002
	p-cresol	106-44-5	Water equilibrated with gasoline	Schmidt et al., 2002
	o-cresol	95-48-7	Water equilibrated with gasoline	Schmidt et al., 2002
	3,4-dimethylphenol	95-65-8	Water equilibrated with gasoline	Schmidt et al., 2002
	2,6-dimethylphenol	576-26-1	Water equilibrated with gasoline	Schmidt et al., 2002
	3,4,5-trimethylphenol	527-54-8	Water equilibrated with gasoline	Schmidt et al., 2002
	2,6-di-tert-butylphenol	128-39-2	Identified additive	Landels, 1995
Benzotriazoles	benzotriazole	95-14-7	Water equilibrated with gasoline	Schmidt et al., 2002
	1-methylbenzotriazole	13351-73-0	Water equilibrated with gasoline	Schmidt et al., 2002
Poly phenol (schiff base)	N,N-disalicylidene-1,2-diaminopropane	94-91-7	Water equilibrated with gasoline	Schmidt et al., 2002
Thiophenes	thiophene	110-02-1	Identified additive	Quimby et al, 1992
	benzothiophene	95-15-8	Water equilibrated with gasoline Identified additive	Quimby et al, 1992, Schmidt et al., 2002
Alcohols	methanol	67-56-1	Fuel ethanol analysis	Weaver et al., 2009
	ethanol	64-17-5	Fuel ethanol analysis	Weaver et al., 2009
	1-propanol	71-23-8	Fuel ethanol analysis	Weaver et al., 2009
	2-propanol	67-63-0	Potential environmental impact	VFJ, 2006
	isobutyl alcohol	78-83-1	Fuel ethanol analysis	Weaver et al., 2009
	2-methyl 1-butanol	137-32-6	Fuel ethanol analysis	Weaver et al., 2009
	3-methyl 1-butanol	123-41-3	Fuel ethanol analysis	Weaver et al., 2009
	2-ethyl 1-hexanol	104-76-7	Potential environmental impact	VFJ, 2006
	2-butoxy ethanol	111-76-2	Potential environmental impact	VFJ, 2006
Ester	ethyl acetate	141-78-6	Fuel ethanol analysis	Weaver et al., 2009
Ester-Acid	1,2-bis(2-ethylhexyloxycarbonyl) ethanesulphonate potassium salt	7491-09-0	Potential environmental impact	VFJ, 2006
Neutral organics	1,1-diethoxyethane	105-57-7	Fuel ethanol analysis	Weaver et al., 2009
	2-ethylhexyl nitrate	27247-96-7	Potential environmental impact	VFJ, 2006
	tetrapropylenebutanedioic acid	27859-58-1	Potential environmental impact	VFJ, 2006
Undesignated	di-sec-butyl-p-phenylenediamine	101-96-2	Identified additive	Owen, 1989

1-propene, 2-methyl-homopolymer, hydroformylation products, reaction products with ammonia	68891-84-9	Potential environmental impact	VFJ, 2006
(Z)-4-oxo-4-(tridecylamino)-2-butenoic acid	84583-68-6	Potential environmental impact	VFJ, 2006
polyolefin mannich base	--	Potential environmental impact	VFJ, 2006

Jim Weaver is a Hydrologist with US EPA and can be reached at weaver.jim@epa.gov. David Spidle is a Research Chemist and can be reached at spidle.david@epa.gov .

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