

# Beyond MSDS: A Review of Hazardous Materials Used by New York's Natural Gas Industry

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September 18, 2009

The New York Department of Environmental Conservation (DEC), in response to a Freedom of Information Law request from the Committee to Preserve the Finger Lakes, sent material safety data sheets (MSDS's) for 48 products permitted for use in the drilling and development of natural gas wells in New York. These are posted online by the Finger Lakes chapter of the Sierra Club:

<http://newyork.sierraclub.org/fingerlakes/gasinfo.html>.

From these and many other documents, Steve Coffman of the Committee to Preserve the Finger Lakes, developed a wonderful article: "The Safety of Fracturing Fluids – A Quantitative Assessment", available at <http://www.preservethefingerlakes.com/id18.html>. In it, he systematically presented the hazards listed in the MSDS's, along the way correlating product names with some of their specific chemical components.

However, Steve's approach had limitations. MSDS's are good at describing the hazards of chemicals or mixtures in their pure states, but they don't tell us much about the health risks of residues where these products are diluted. They also don't help much to assess relative risks – which products are more or less dangerous than others.

A particular problem with MSDS's submitted by energy industry representatives is that many of them do more to hide chemical composition than to reveal it. Their intentionally vague language reminded me of that generally found in patents, where the goal is to protect as much intellectual turf surrounding an invention as possible. Therefore, I researched patent applications related to these products, where the actual chemicals in use are usually listed as the most "preferred embodiment" of each protected idea.

In this article I will draw connections between different terms used for identical compounds, point out families of chemicals that have similar properties, and offer toxicity information that delves deeper than typical material safety data sheets (MSDS's). In addition to MSDS's and patents, I've consulted various texts and

dissertations, peer-reviewed journal articles, reports from the Environmental Protection Agency (EPA), the Food and Drug Administration (FDA), the National Toxicology Program (NTP), the Centers for Disease Control (CDC), and related agencies in Canada and Australia where available. The Endocrine Disruption Exchange (<http://www.endocrinedisruption.com/home.php>) has been a major information resource. Please note that my comments should be considered in addition to MSDS's, not in isolation from them.

Now, on to the materials :

## Biocides

### **1. MAGNACIDE 575**

This product contains bis[tetrakis(hydroxymethyl)phosphonium] sulfate.

Bis[tetrakis(hydroxymethyl)phosphonium] sulfate was first used as a flame retardant for cotton fabrics, called Retardol S. Since its use as a biocide is fairly recent, toxicity studies are incomplete. It is known to be highly toxic to aquatic organisms, and is suspected to promote cancer in rodents. Its toxicity in mammals is selective for liver tissue. However, compared to the other biocides in this list, it is probably the easiest for humans to handle with relative safety.

### **2. BIO CLEAR 200**

This breathtakingly toxic mixture of 2,2-dibromo-3-nitrilopropionamide (DBNPA) with polyethylene glycol (PEG) behaves differently in different organisms. The decomposition products noted in the MSDS arise from metabolism in microbes and many aquatic organisms. (In fact, DBNPA is damaging or lethal to brown trout, *Daphnia magna* and bay oysters at concentrations so low they cannot be chemically detected.) However, in mammals, this mixture chiefly leads to formation of aldehydes which stress antioxidant defenses, particularly enzymes called glutathione-dependent peroxidases. Therefore, chronic exposure should be expected to influence aging in humans.

Polyethylene glycol is essentially non-toxic; it's used solely to thicken the solution.

### **3. BE-3S**

This product contains 2-bromo-3-nitrilopropionamide and 2,2-dibromo-3-nitrilopropionamide.

This mixture of the biocide 2-bromo-3-nitrilopropionamide (BNPA) with the related chemical DBNPA (discussed above) has essentially the same toxicity profile as DBNPA alone: very severe, especially for aquatic organisms.

#### **4. BE-6**

This product contains 2-bromo-2-nitro-1,3-propanediol.

The biocide 2-bromo-2-nitro-1,3-propanediol (BNPD) presents human health hazards similar to BNPA and DBNPA, above, except that *it is also a suspected carcinogen*. However, it is much more harmful to aquatic organisms than BNPA or DBNPA – and they are highly toxic to aquatic organisms. This is a terrible environmental poison.

#### **5. ALDACIDE G**

This product contains glutaraldehyde.

The biocide glutaraldehyde is extraordinarily poisonous: harmful if inhaled or absorbed through the skin. It is capable of causing permanent eye damage upon exposure, and can cause potentially lethal chemical pneumonia if lung tissue is exposed (e.g., after deep aspiration). Harmful exposure levels for mammals extend as low as 50 parts per *billion*.

### Corrosion Inhibitors

#### **6. CORROSION INHIBITOR A261**

This product contains aromatic ketones, aliphatic alcohol polyglycol ether, methanol, aliphatic acid, aromatic hydrocarbons, formaldehyde and propan-2-ol.

Aromatic ketones (most likely acetophenone or 3-hydroxy-1-phenylpropan-1-one, which comprise the bulk of this product) tend to be much less hazardous than aromatic hydrocarbons such as benzene, ethylbenzene, toluene and xylenes (BTEX), which are all highly toxic, especially to liver tissue, at very low concentrations. Aromatic hydrocarbons also tend to be carcinogenic (they promote cancers), at low doses.

The term “aromatic” (in aromatic ketones and aromatic hydrocarbons) refers to a set of shared chemical characteristics, not how these chemicals smell.

Aliphatic alcohol polyglycol ether refers to a family of compounds, not a single pure substance. Most of them are non-ionic surfactants of low toxicity, although this cannot be said for certain glycol ethers, to which they are chemically related.

Methanol and formaldehyde were discussed above.

Propan-2-ol is another name for isopropyl alcohol, also known as 2-propanol or rubbing alcohol. It is much less toxic than methanol, and is a minor component of this product.

“Aliphatic acid” is a non-specific term that refers to a one or more fatty acids extracted from coconut or rapeseed oil. Its hazard is negligible.

#### **7. FE-5A**

This product contains thioglycolic acid.

Thioglycolic acid is best known as that terrible-smelling chemical used by cosmetologists to straighten unruly hair. While it is certainly hazardous in concentrated form, its use by natural gas operators as a corrosion inhibitor doesn’t pose much risk to health. Besides, its wretched odor tends to alert people to spills or other accidental releases.

#### **8. FR-46**

This product contains ammonium bisulfate.

Ammonium bisulfate has been used with thioglycolic acid (above) as a hair-care agent. While it is very corrosive in a concentrated state, our greatest health concern would be with chronic exposure to it: This salt tends to accumulate in tissues, especially lung and mucous membranes. Therefore, its use as a corrosion inhibitor in gas extraction poses moderate hazard.

#### **9. CL-14**

This product contains methanol and propargyl alcohol.

Propargyl alcohol is the greater hazard here; so bad that, according to industry advertisements (for other products), oil and gas field workers have complained about having to work with it. Exposure to it causes awful respiratory, skin and eye symptoms, and many of these persist long after exposure has stopped. Propargyl alcohol can accumulate in liver, kidney, arterial, bronchial and brain tissues, to cause multi-organ chronic health problems.

This chemical is significantly toxic to aquatic organisms, especially fathead minnows and daphnids; however, it is rapidly biodegraded in water or soil.

Propargyl alcohol and prop-2-yn-1-ol (next section) are different names for the same chemical; a third name often encountered is acetylenic alcohol.

Methanol (also known as methyl alcohol or wood alcohol) is rapidly metabolized by most organisms to formaldehyde, which is a really dangerous poison known to cause long-lasting skin and respiratory tract damage. At extremely low concentrations, formaldehyde can also promote a variety of cancers.

#### **10. HAI-OS ACID INHIBITOR**

This product contains propargyl alcohol and methanol, discussed above.

### Surfactants

#### **11. FR-48**

This product is claimed to contain no hazardous substances. From the physical description, it is most likely a microemulsion of acrylic beads in water.

#### **12. FLOWMAX 50 (Two related MSDS's)**

This product contains isopropyl alcohol, limonene, and a non-ionic surfactant.

Isopropyl alcohol (a secondary alcohol, as listed in one of the MSDS's) was discussed above.

One of the proprietary constituents of this product is limonene, the chief component of lemon oil. Limonene is very familiar to gas industry operators, since many natural gas

odor markers consist of sulfur compounds derived from it. Limonene is non-toxic as used.

The other proprietary constituent is an unspecified non-ionic surfactant. All the choices listed in the patent, however, exhibit low toxicity.

### **13. Ezeflo F108 Surfactant**

This product contains a proprietary amine derivative.

The “amine derivative” in this product is a cationic gemini surfactant. This bears some explanation. In the mid-1980's, Dow Corning developed the viscoelastic surfactant erucyl-bis(2-hydroxyethyl) methylammonium chloride, which was mixed with isopropyl alcohol and trademarked by Schlumberger as ClearFRAC. This product was relatively safe for handling by humans, but sufficiently toxic to algae and other marine organisms that it was restricted or banned by Scandinavian countries.

By cross-linking this (and similar) compounds with epichlorohydrin, scientists in Australia produced the first cationic gemini surfactants. Their greatest advantages are that they viscosify (thicken) solutions (similarly to ClearFRAC) at one-tenth the concentration needed for that agent. However, these “gemini quats” are also toxic to algae, and they have not been sufficiently tested for biosafety with us or our environment to be assessed.

### **14. FAW-5**

This product contains 2-butoxyethanol, methanol, ethyl alcohol and ammonia.

2-Butoxyethanol is the major threat in this product. The MSDS details its devastating effects at high concentrations, but at vanishingly small concentrations it still promotes infertility, birth defects and rare adrenal tumors. Women are at special risk, somewhat of a surprise to toxicologists who first uncovered its reproductive effects in *male* rats.

2-Butoxyethanol is a glycol ether, a member of the family of chemicals noted just above. *Some* members of this chemical family are not highly toxic; they are commonly used as non-ionic detergents.

Ammonia is a potent toxin, but people generally respond to its familiar acrid odor by getting out of its way. This effectively limits the danger it poses.

Methanol (discussed above) is another word for methyl alcohol, also known as wood alcohol. Ethanol is another word for ethyl alcohol, also known as grain alcohol or just “alcohol”. 2-Propanol (also discussed above) is another word for isopropyl alcohol or rubbing alcohol. This kind of terminology is typical for these liquids.

#### **15. INFLO-102**

This product contains methanol, isopropanol and 2-butoxyethanol, discussed above.

#### **16. MULTIFUNCTIONAL SURFACTANT F105**

This product contains two proprietary polyethoxylated alkanols, 2-butoxyethanol and butan-1-ol.

The term “polyethoxylated alkanol” refers to a family of glycol ethers used as non-ionic surfactants which, in this particular product, are moderately toxic.

Butan-1-ol, also known as butanol or butyl alcohol, is more dangerous than the alcohols discussed above, because it is an endocrine disruptor at very low concentrations.

2-Butoxyethanol was discussed above.

### Lubricants

#### **17. ACTIVATOR 78-ACTW**

This product contains secondary C12-14 ethoxylated alcohols and methanol.

These low molecular weight fatty alcohols are typically extracted from fats rather than synthesized, and the number of ethoxy functional groups may vary; therefore, they comprise a family of molecules, not a single pure substance. Even though this mixture of glycol ethers is hazardous in concentrated form, the product as used is only moderately toxic. It is moderately biodegradable as well.

Methanol was discussed above.

#### **18. LGC-35 CBM**

This product contains paraffinic solvent and polysaccharide.

Paraffinic solvent is probably best known as mineral spirits, also called deodorized kerosene or hydrotreated light petroleum distillate. If lung tissue is exposed, this solvent can induce potentially lethal chemical pneumonia, but the major target organ appears to be the liver, where chronic exposure to low doses may promote cancer. Kerosene is harmful to amphibians and many aquatic organisms, and is not very biodegradable.

Polysaccharide in this product is guar gum. This carbohydrate is non-toxic, but its use as a viscosifier (thickener) requires addition of a borate-based cross-linker, which introduces reproductive toxins to the mix. Further, since this starch is a favorite food for bacteria, algae and fungi, its use also requires significant addition of biocides.

#### **19. FRW-14**

This product contains hydrotreated light distillate and ethoxylated alcohol.

Hydrotreated light distillate, better known as deodorized kerosene, was discussed above.

Ethoxylated alcohol refers to a range of glycol ethers, discussed above.

#### **20. Water Friction Reducing Agent J313**

This product contains hydrotreated light petroleum distillates and ethoxylated octylphenol.

Hydrotreated light petroleum distillates, better known as deodorized kerosene, were discussed above.

Ethoxylated octylphenol is an aromatic glycol ether, better known (to biochemists, anyway) as Triton X-100. It is only mildly irritating to humans, but is highly toxic to aquatic and marine organisms, particularly salmon, cod and shrimp.

#### **21. SANDWEDGE WF**

This product contains heavy aromatic petroleum naphtha, methanol and isopropanol.

“Heavy aromatic petroleum naphtha” refers to polycyclic aromatic hydrocarbons (PAH’s), which are extremely dangerous environmental toxins. They are biodegraded very slowly, and are potent human carcinogens at very low levels of exposure.

Methanol and isopropanol were discussed above.

### Cross-Linkers

#### **22. FDP-S798-05**

This product contains sodium perborate tetrahydrate.

Sodium perborate tetrahydrate can be really corrosive in concentrated form, but it is not much of a health threat as used by gas industry operators. It is a moderate oxidizing (bleaching) agent, not as harsh at low concentrations as hydrogen peroxide.

#### **23. OptiKleen-WF**

This product contains sodium perborate, discussed above.

#### **24. BORATE CROSSLINKER J532**

This product contains aliphatic polyol and sodium tetraborate decahydrate.

The “aliphatic polyol” is most likely glycerol. It is practically non-toxic.

Sodium tetraborate decahydrate is better known as borax. It has been shown to be a significant reproductive poison implicated in infertility and birth defects.

#### **25. BC-140**

This product contains monoethanolamine, ethylene glycol and boric acid.

The major health and environmental threat in this mixture is ethylene glycol, discussed above.

Monoethanolamine , or simply ethanolamine, and boric acid are both corrosive in high concentrations. They are fairly tame at moderate to low concentrations. However,

boric acid has been used for many years as a roach and ant pesticide, occasionally poisoning young children who eat it.

#### **26. FE-1A**

This product contains acetic anhydride and acetic acid.

Acetic anhydride is an incredibly reactive chemical, so in high concentrations it is extremely hazardous. However, by reacting with just about everything (including the compounds it was meant to derivatize), it quickly degrades, and therefore tends to pose no chronic health threat.

Acetic acid is what gives vinegar its flavor; it is of little concern as used in this product.

### Breakers

#### **27. CLA-STA XP Additive**

This product contains polyepichlorohydrin trimethylamine quaternized.

Polyepichlorohydrin trimethylamine quaternized is a flocculent designed to “break” (clarify) solutions thickened by advanced viscosifiers called cationic gemini surfactants. Recently developed in Australia, its biological safety has not been studied in any detail.

#### **28. GBW-30 Breaker**

This product contains hemicellulase enzyme and carbohydrates.

Hemicellulase is an innocuous enzyme also used in baking and paper manufacturing.

The specific carbohydrates aren’t listed, but are unlikely to be hazardous.

#### **29. Breaker J218**

This product contains diammonium peroxydisulfate.

Diammonium peroxydisulfate is a corrosive oxidizing agent which is irritating in concentrated form, but its major health threat arises from its ability to cause allergic sensitization upon repeated exposure.

## Scale Inhibitors

### **30. FERROTROL 300L**

This product contains citric acid, which is non-toxic unless very high concentrations are involved. As used for inhibiting iron-based scale formation, it is of little concern.

### **31. HC-2**

This product contains sodium chloride and inner salt of alkyl amines.

Sodium chloride is our familiar “table salt”; it is not hazardous as used in this product.

The term “inner salt of alkyl amines” refers to a family of chemicals called chelating agents. They are used to break down scale that has built up in well bores, pipes, etc.

In high concentrations, these chemicals are health hazards because they trap metal ions (such as calcium, magnesium and iron) needed for many body functions. At low concentrations, they pose some risks to aquatic and soil organisms. Because this product contains a variety of chelators, including EDTA, NTA, DTPA and others, I can't offer a more specific hazard assessment.

### **32. SCALEHIB 100**

This product contains ethylene glycol.

Ethylene glycol is the primary chemical in automobile antifreeze. This is not to suggest that it's not hazardous: It can accumulate in kidney, liver, and brain tissues, and it is a carcinogen. What's worse, it has a sweet taste, which promotes its ingestion by cats and other domestic animals.

## Clay Stabilizers

### **33. TEMPORARY CLAY STABILIZER L64**

This product contains tetramethyammonium chloride (TMAC).

Tetramethylammonium chloride is the most basic of the quaternary alkyl amines, a reactive family of chemicals often used as microbicides. This product is very poisonous, made worse by the fact that it has practically no odor. It is biodegraded in water or soil very slowly.

Most of the newest slickwater surfactants (such as ClearFRAC and cationic geminis) are members of this family of compounds, but they are all much less hazardous than TMAC.

#### **34. Clay Treat 3C**

This product contains tetramethylammonium chloride, discussed above.

### Gelling Agents

#### **35. FRP-121 (Two related MSDS's)**

This product contains anionic polyacrylamide. Beyond its ability to irritate the eyes and mucous membranes, this material is pretty non-toxic.

#### **36. FRW-14**

This product contains unspecified carbohydrates. The product itself is non-toxic, but as noted above, use of starch-based gelling agents requires the accompanying use of cross-linkers and biocides.

#### **37. WATER GELLING AGENT J580**

This product contains unspecified carbohydrates, discussed above.

### Conditioners / Other

#### **38. LP-65**

This product contains ammonium chloride.

Ammonium chloride can irritate the skin, eyes and respiratory tract in concentrated form, but is on the low end of the toxicity spectrum as used.

### **39. GAS PERM 1000**

This product contains isopropanol, discussed above.

### **40. FDP-S819**

This product contains isopropanol, discussed above.

### **41. HYDROCHLORIC ACID (Three related MSDS's)**

Also known as muriatic acid or stomach acid, this is a very strong acid, even at fairly low concentrations. The solutions used by gas extraction operators are much more concentrated than what is found in your stomach. Its health effects are related to its corrosiveness to tissues.

### **42. FE Acid**

This product contains hydrochloric acid, discussed above.

### **43. LIQUID NITROGEN**

This is an extremely cold liquid, which is practically its only hazardous property. However, in enclosed spaces, its vapor can pose an asphyxiation hazard.

I trust that this article will serve to illuminate our public discourse about materials used in New York's natural gas industry. Please get in touch with me through Sustainable Otsego ([www.sustainableotsego.org](http://www.sustainableotsego.org)) with any comments, corrections or questions.

Respectfully,

Ron Bishop