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The Hazardous Material Information Resources System

By Linwood Gilman and Steve Perez, DLA Aviation, Hazardous Information Program Division

DLA Aviation Richmond is home to the functional management of DoD's electronic repository for hazardous materials information. The repository is called the Hazardous Material Information Resource System (HMIRS), and was previously known as the Hazardous Material Information System (HMIS) when it was established on April 1, 1978.

Department of Defense Instruction (DoDI) 6050.05 is the document that spells out the DoD Hazard Communication (HAZCOM) Program, and prescribes the requirements for how HMIRS is to operate. It designates DLA as the lead component for HMIRS, the central repository for Material Safety Data Sheets (MSDSs), and related data for the military services and civil agencies.

A MSDS contains information that includes the chemical composition and hazardous communications information that is needed to comply with the Occupational Safety and Health Administration's (OSHA's) Hazard Communication Standard (29CFR1910.1200). The purpose for the MSDS is to ensure that the hazards of all chemicals produced or imported are evaluated, and that information concerning their hazards is transmitted to employers and employees.

HMIRS assists Federal government personnel who handle, store, transport, use, or dispose of hazardous materials to adhere to OSHA regulations, thus avoiding fines or other legal actions. HMIRS is a data management system for the storage and retrieval of data on products used by DoD personnel (civilian, sailors, soldiers, airmen) in the field when they have questions concerning a product. It makes MSDS, transportation,

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disposal, environmental, contract, and label information accessible by national stock number, local item identification number, contract number, product identity, trade name and/or part number, MSDS serial number and manufacturer/contractor commercial and government entity code (CAGE).

A commercial off the shelf (COTS) software product called ProSteward is HMIRS's operating system. HMIRS consists of an input product, the Online Administrator utilized by the HMIRS focal points, and an output product, the HMIRS Web (http://www.dlis.dla.mil/hmirs) for the user community.

In HMIRS, product records are made up of two portions, Value Added data and supporting documentation. The documents may be MSDSs, Manufacturer's Labels, Product Sheets and other relevant (e.g. transportation, disposal etc.) document types. These documents provide the HMIRS user with vendor supplied information, about a vendor supplied product, thereby allowing the user to meet regulatory and service/agency regulation requirements. Value Added data are made up of select fields taken from the MSDS, government unique information or other documentation that are addressable and that can be searched or transmitted electronically to other systems. Most importantly, the chemical composition information of the purchased product is part of the Value Added information, and is crucial in the management of hazardous materials as well as in complying with environmental and disposal regulations.

Service/Agency focal point personnel review documents and enter information into HMIRS at the following locations: DLA's Safety and Health, as well as Transportation focal point at DLA Aviation (DSCR-VBA); Navy's Safety and Health focal point at Navy and Marine Corps Public Health Center; Navy Transportation focal point at Navy Operational Logistics Support Center; Air Force's Safety and Health focal point as well as Transportation focal point at Wright Patterson AFB; Army's Transportation focal point at LOGSA PSCC, Tobyhanna AD, and GSA's Safety and Health focal point at the Heartland Supply Operations Center.

The program is managed by a Program Manager, and a Functional Manager. The Program Manager's Office (PMO) for HMIRS is in Battle Creek, MI., and the Functional Manager's Office (FMO) is in Richmond, VA.

The FMO communicates with the focal points, and gathers requirements for modifications to the online program that are driven by regulatory changes. Modifications and/or changes are made, as necessary, to make data entry easier and the product better for the users. The FMO coordinates any changes between the software developer and the Military/Agency requester(s). Since the input product is a COTS package, coordination must also be done in concert with the commercial users.

The current "high visibility" efforts on the horizon for HMIRS are the accommodation of the additional data required by the Global Harmonization System (GHS), and the European Union's Registration, Evaluation, Authorization, and Restriction of Chemical substances (REACH).

DoT News

Air Force and Navy Developing Alternative Sources of Jet Fuel

By Philip Saunders, Chemical Engineer, HTIS

A recent discussion on National Public Radio (NPR), that is available at its website, highlights efforts by the Air Force and Navy to develop jet biofuels produced from renewable sources. The Navy's current goal is to ensure that 50 percent of the fuel for its aircraft and surface ships comes from renewable (non-petroleum) sources by 2020. The Air Force has set a similar goal for fueling its aircrafts, but the Air Force's target date is 2016. While these goals are often touted for being 'green', they really originate from strategic and national security considerations because much of the nation's oil consumption comes from foreign and sometimes volatile sources. Dependence on oil from these sources could make our armed forces vulnerable to rapid fuel price increases and shortages, if events in that area of the world disrupt shipments from those locations.

There are currently two approved routes for the generation of aviation biofuels: one involves the conversion of vegetable oils and animal fats to a biofuel, and the other is a process using biomass solids to generate pyrolysis oil or syngas. Much of the NPR report focuses on the use of vegetable oil that is extracted from the camelina plant, and converted into bio-derived synthetic kerosene. The synthetic fuel generated from this plant is virtually indistinguishable from other jet fuels, but most vegetable oils and animal fats can be refined to produce similar fuels. In this case, the focus is on camelina because the plant has high oil contents and can be planted on fallow farmland, so there is no need for a trade-off between putting food on the table or fuel in the tank.

Since traditional petroleum jet fuels and biobased jet fuels are functionally identical, their combustion will generate equivalent amounts of carbon dioxide (CO_2). The environmental advantage of using biofuels originating from plants is that the carbon in the biofuels was removed from the air as the plants grew, whereas the carbon from petroleum fuel originated under ground. Some reports have cited an 80% reduction in greenhouse gas emissions when using biofuels produced from the camelina, but this is an oversimplification, because the back-end carbon dioxide emissions are unchanged. It is only when considering the entire plant-fuel-carbon-plant life-cycle that the 80% reduction claim is valid, since the carbon is essentially being recycled.

Despite the potential environmental benefit of using biofuels generated from vegetable oils, their use remains somewhat controversial with some environmentalists. The controversy is because the increased usage of such oils for fuel drives up their prices, and can lead to the destruction of rain forests as

farmers convert rain forest to farm land in an effort to cash in on the high prices of the plants. In addition, many of these plants are also food crops, and increasing the demand for those plants may cause food shortages and the associated price increases as well. One alternative to growing crops for their oils is the use of waste fats such as that from used cooking oil or greases. The primary objection to focusing on this approach is that the quantities in which this waste is generated are not large enough to account for more than a small fraction of current fuel demand.

In addition to the use of vegetable oils and animal fats, much research has been done on the production of aviation fuels from solid biomass. This can be accomplished through the use of pyrolysis of the biomass into a condensable pyrolysis oil that can be further refined into jet fuel, or through gasification of the biomass to syngas (a mixture of hydrogen and carbon monoxide). Syngas can be used as a feedstock for a catalytic reaction called the Fischer-Tropsch process that produces synthetic kerosene that can be used as jet fuel.

Other methods of producing biofuels have been explored over the last decade, but have been less successful for various reasons. One of these methods involved thermal depolymerization to convert organic agricultural waste to a form of diesel oil. This process uses heat and pressure to mimic the geological process that naturally produces petroleum oil in the ground. One such plant in Missouri used the waste from a turkey processing facility, and was economically viable when oil prices were elevated. However, the plant was forced to shut down temporarily after local residents complained of foul odors emanating from the facility. The company was eventually forced to declare bankruptcy due to various lawsuits, as well as a drop in oil prices, resulting in the process being economically unfavorable.

Regardless of the method used to generate alternative sources of jet fuel, the challenge still remains to make such sources economically comparable to traditional petroleum fuels. This is not yet the case, but the armed services hope that by cultivating the technologies and know-how, the industrial base will be able to ramp up its production, and reduce production costs should a petroleum shortage or price increase ever make biofuels an attractive option.

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4. "Fat to Jet Fuel". **Online Ref:** http://www.isa.org/Printer-Template.cfm?Template=/ContentManagement/HTMLDisplay.cfm&ContentID=59929&FuseFlag=1

5. "Biofuel for Jets Could Cut Carbon Emissions Over 80 Percent" by Marcia Goodrich, Michigan Tech, May 9, 2009. **Online Ref:** http://www.rdmag.com/News/2009/06/Energy-Biofuels-Could-Lighten-Jet-Fuel-Carbon-Footprint/

6. "5 Things You Need to Know About The Fischer-Tropsch Process" by Bill Siuru, Green Car Journal, July 3, 2008. **Online Ref:** http://www.greencar.com/articles/5-things-need-fischer-tropsch-process.php

Environmental News

Correlation Analysis of VOCs in Federal Acquisition Service* — **Procured Sealants and Adhesives versus Regulatory Specifications**

By Luke Shokere, Chemist and Randall Schober, Environmental Programs, Branch Chief, Heartland Supply Operations Center, FAS, Kansas City, MO*

Introduction

Volatile organic compounds (VOCs), such as dichloroethane, cyclohexane, and toluene, although necessary in the formulation of high-performance sealants and adhesives, are a source of air pollution and physiological toxins. When used indoors, these materials directly expose end-users to the VOCs emitted during application of the product. As a means of reducing toxigenic exposures, one approach has been to specify and implement an "upper-limit" on the VOC levels that comprise their formulations. The VOC regulatory specifications developed and implemented by the California Air Resources Board (CARB) provide a suitable standard for assessing progress because they:

- Pertain specifically to the VOCs in consumer products;
- Are expressed in units of "% weight VOC" for validity of inter-product comparisons; and,
- Are progressively stringent over time.

Using the CARB regulatory values for VOC as a reference, our current objective is to depict the VOC levels found in the high-performance sealants and adhesives procured by the Federal Acquisition Service (FAS).

Analytical Method

The Heartland Supply Operations Center of the FAS procures

varied materiel for the DoD, and among these are high-performance sealants and adhesives. For this study we purposefully selected two major suppliers (Supplier A and B) from our database, because of their broad inter-class range of products, thereby addressing sample representativeness (i.e., product type variation). The product's Material Safety Data Sheet (MSDS) or Technical Data Sheet (TDS) was the source of the VOC levels, typically determined by ASTM D 3960 or the California SCAQMD Method 316 B. Since manufacturers rarely report the "net" weight (VOC, less water and exemp-ted solvents), but do provide the "gross" weight (total VOC), we further analyzed the "weight of total VOC" values (g/L or lbs/gal) because of the latter value's reliability. The CARB VOC specifications were cited in units of "percent weight VOC"; therefore, we converted the VOC values on the technical documents into "% wt. VOC", using appropriate conversion factors. Finally, we prepared scatter plots (Figures 1 and 3) and histograms (Figures 2 and 4) to assess correlations between the observed values and the upper-limit specification. Each data point in Figures 1 and 3 represents a sealant or adhesive product that is traceable to a National Stock Number (NSN). The percentage values in the histograms (Figures 2 and 4) were computed by dividing the number of compliant or non-compliant NSNs by the total number of NSNs for a particular product type, then multiplying by 100%.

Results

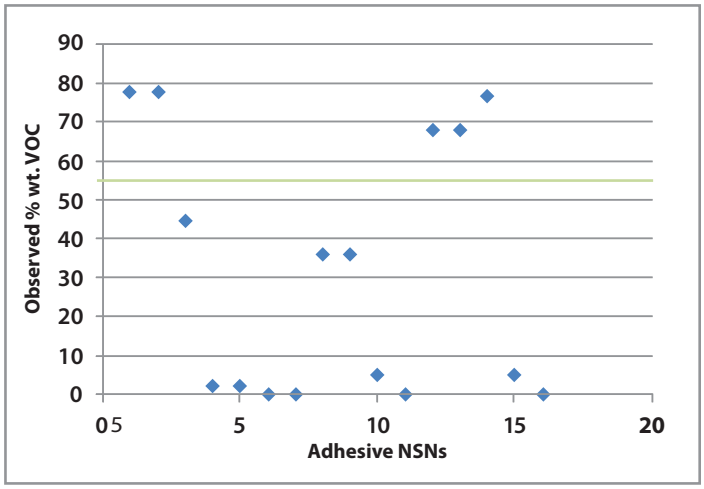

Figure 1. Scatter plot of % wt. VOC from all adhesives (NSNs) procured from Supplier A. Green line represents the CARB upper-limit % wt. VOC value for adhesives (note: single adhesives supplier).

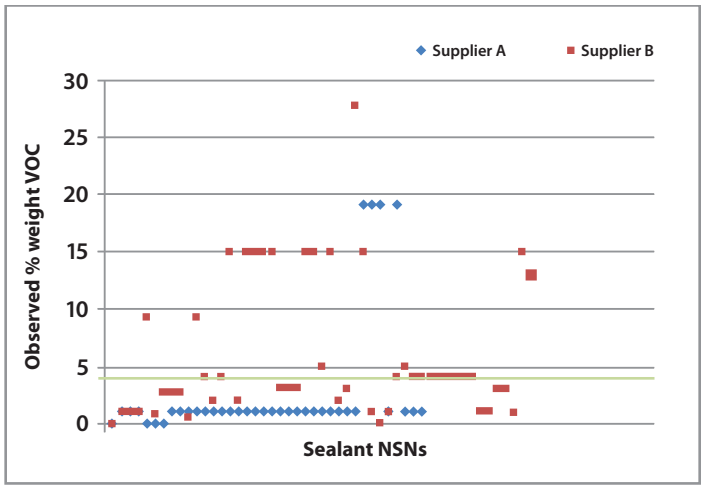

Figure 3. Scatter plot of % wt. VOC from all sealants (NSNs) procured from Suppliers A & B. Green line represents CARB upper-limit % wt. VOC value for sealants.

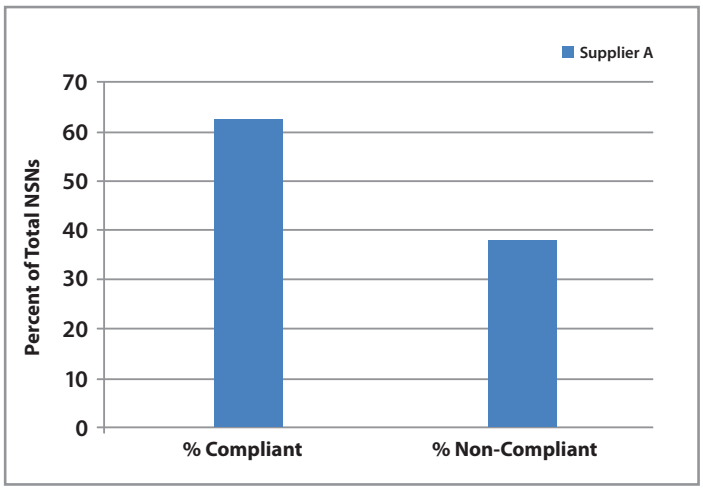

Figure 2. Histogram of adhesives scatter plot results (Fig. 1).

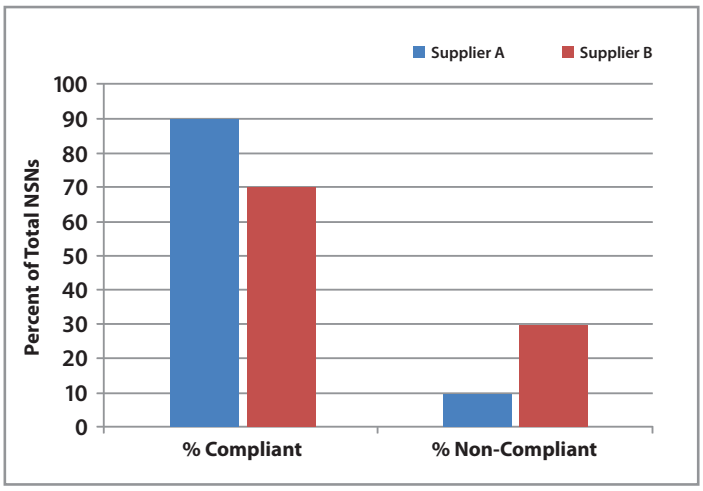

Figure 4. Histogram of sealants scatter plot results (Fig. 3).

NSN	Observed % wt. VOC	CARB % wt. VOC Spec	Low VOC Compliant	Explanation
8030-xx-xxx-xxx1	100	4	Yes	Exempted Solvent
8030-xx-xxx-xxx2	100	4	Yes	Exempted Solvent
8030-xx-xxx-xxx3	100	4	Yes	Exempted Solvent

TABLE 1. Regulatory-exempted solvent in three sealant formulations from Supplier A.

Analysis of Results

The majority of adhesives (Figs. 1 and 2) procured from Supplier A had VOC levels that were below the regulatory value (55% wt. VOC), and could, therefore be genuinely classified as "Low VOC". In the 37.5% of adhesive NSNs that were non-compliant, a common factor was that they were comprised of binary kits. Furthermore, when we examined the formulations we observed that the "accelerator" part of the kit contained elevated levels of non-exempt solvents (e.g., toluene). The majority of sealants (Figs 3 and 4) procured from both suppliers had VOC levels that were in compliance with the regulatory value (4% wt. VOC). Supplier A demonstrated greater compliance than Supplier B. After examining the sealant formulations of both suppliers, we found that the predominant number of non-compliant NSNs occurred in sealants that consisted of binary kits wherein the "accelerator" portion was often elevated in non-exempt solvents. Acetone is considered by CARB and the EPA to be an "exempt solvent" due to its low toxigenicity and negligible photoreactivity. During the review of technical documents, we noted that several sealants contained 100% VOC (Table 1); however, because the VOC was acetone its value was assigned as "0% wt. VOC" in the data analysis (Figure 3).

Implications of the Findings

Binary adhesives and/or sealants, consisting of a separately packaged resin and high vapor-pressure accelerant, are valued for their fast curing times and exceptional performance. The current results showed that these types of materials are frequently responsible for the failures in VOC compliance due to their elevated levels of non-exempt solvents. Innovations in formulation chemistry that utilize either lower concentrations of non-exempt solvents or replace them with exempted solvents should, likely, improve the correlation with the specifications.

Executive Order 13514 established "sustainability" as a Federal procurement initiative; therefore, correlation analyses such as those presented here provide a preliminary means of measuring progress towards achieving this objective. With due consideration of the delimitations of this study, the present results indicate that FAS has made reasonable progress in procuring "Low VOC" high-performance sealants and adhesives for DoD applications. Future studies will involve correlation analyses of other suppliers in the FAS database. Additionally, FAS is interested in assessing concordance between trans-national VOC standards (e.g., European Union) versus those in the US.

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1. Determining VOC Content, Solvents Council Bulletin, October 1999.

2. An Introduction to Indoor Air Quality: Volatile Organic Compounds. Environmental Protection Agency, http://www.epa.gov/iaq/voc2.html

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EPA's Green Products Web Portal

By Abdul H. Khalid, Chemical Engineer, HTIS

The Environmental Protection Agency (EPA) recently launched the "Green Products Web Portal", a tool designed to help "the user navigate the increasingly important and complex world of greener products. It allows users to search for the EPA programs related to greener products based on the type of user and their specific product interests. It also provides links to additional greener products information from the EPA and other sources". The new green products web portal is available at: www.epa.gov/greenerproducts.

According to Mr. Steve Owens, Assistant Administrator of EPA's Office of Chemical Safety and Pollution Prevention (P2), "the green products web portal is an easy way to become familiar with products that prevent pollution and protect our environment. By purchasing greener products, consumers help reduce air pollution, conserve water and energy, minimize waste and protect their children and families from exposure to toxic chemicals, while also creating green jobs. P2 is good for our health, our environment, and our economy".

Manufacturers of green products generally, attach "Eco-labels" to their products so that the consumers know that the products meet certain standards. These standards can be developed by private entities, by public agencies under their authorities, or jointly by stakeholders and experts from the public and private sectors.

As part of its mission, the EPA works with a variety of non-government standards developers to promote the development of voluntary consensus standards for environmentally preferable goods and services. The National Technology Transfer and Advancement Act (NTTAA) and OMB Circular -119 direct the Federal government to use and participate in

the development of reference standards in voluntary consensus processes that also meet government needs.

The EPA develops standards, criteria documents, and Eco-labeling programs for products as part of its mission to protect human health and the environment. Examples of the EPA's Eco-labeling programs that illustrate Federal leadership in advancing energy efficiency, water efficiency, and green chemistry are:

- Energy Star (ES);
- Water Sense (WS); and,
- Design for the Environment (DfE).

In recent years, a growth in demand for "green products" has led to an uncertainty about the environmental claims associated with standards and labels. In response to these concerns, the Federal Trade Commission (FTC) created its "Green Guide" that can be found at: http://www.ftc.gov/bcp/grnrule/guides980427.htm. This guide ensures that marketing claims regarding the environmental attributes of products are truthful and substantiated. However, these guides largely address, when and how, very specific and narrow environmental attributes can be claimed, not how to construct a broad-based environmental standard or Eco-labeling program.

To facilitate the product-related acquisition goals of Executive Order 13514 (sections 2 and 13), the EPA and GSA co-chair a Product Standards and Eco-labels Subgroup that includes representatives from DoD, USDA, NIST, NIOSH, VA, NASA, DOC, DOL, and other federal agencies involved in developing guidelines for selecting environmental sustainability standards and/or eco-labeling. During the fall of 2011, the subgroup contacted key stakeholders to gain critical input on the development of the guidelines and potential implementation approaches to recommend in the subgroup's report. In early 2012, there will be a comment period announced in the Federal Register to gain further public input.

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Environmentally Preferred Aircraft Spot Cleaners Available Under MIL-PRF-85570

By Moraima Lugo-Millán, Chemist, DLA Aviation, Hazardous Minimization and Green Products

Aircraft spot cleaners that meet MIL-PRF-85570 (Cleaning Compounds, Aircraft, Exterior) requirements, that are more environmentally responsible, and that are also easier to use, are now available through the Defense Logistics Agency (DLA) Aviation Supply Chain. These field tested products are used to clean weapon systems in DoD maintenance facilities, and are on a Qualified Product List (QPL). The new products are available in a concentrated (pre-diluted) form, as an aerosol, and in pre-saturated wipes.

Naval Air System Command (NAVAIR) at Patuxent River, Maryland, partnered with DLA Aviation in Richmond, Virginia to evaluate MIL-PRF-85570 cleaners, and to qualify more environmentally sustainable versions for Type I (General purpose, aromatic solvent base) and Type II (General purpose, Non-solvent) cleaners. The Type I cleaner meets requirements as an aerosol and also as pre-saturated wipes, while Type II meets requirements as a pre-diluted and ready-to-use (RTU) product.

The Type I cleaning compounds, in aerosol and pre-saturated wipes, provide the war-fighter qualified, convenient products to support their corrosion control maintenance requirements while deployed anywhere in the world. Before these new products were available, maintainers were experiencing a lack of acceptable, qualified aircraft spot cleaners, and were using unauthorized products with high solvent content that created health, safety and corrosion concerns. When tested on aircraft, the cleaning effectiveness of the new aerosol product was identical to the unauthorized and widely used MIL-C-43616 aerosol. The new aerosol version replaced the unauthorized and more polluting, high solvent legacy cleaners. The saturated wipes provide the advantages of being conveniently packaged with discrete amounts of the cleaner on each wipe, and producing minimal waste that saves on chemical usage and disposal into the environment.

Ready to use (RTU) Type II cleaners are very convenient, effective, and easy to use across DoD platforms. Previously, these cleaners were purchased in a bulk concentrated form, and aircraft maintainers had to dilute the solution to the appropriate concentration before it was used. Having to dilute the cleaner presented numerous safety, environmental and logistical challenges, especially in remote, dry regions of the world, where clean, potable water is not always available.

Field testing the new products involved determining the cleaning performance of the candidates at various military sites (Oceana, North Island, Norfolk, Andrews JRB, and Key West). Both types of products provided great environmental and logistical benefits to the warfighter. Listed at the top of the next page, are the cleaners that provided successful results with positive feedback, and were also qualified for use. The Qualified Products Database has been updated with these new products.

The NAVAIR 01-1A-509 Cleaning and Corrosion Control Manual and MIL-PRF-85570 specification have been revised and include the new qualified products. The following four NSNs have been created and are available through DoD E-Mall or

TYPE	PRODUCT	MANUFACTURER
Type I	PENAIR M5571 CEE-BEE R-681	Penetone Corporation Carlstadt, NJ 07072-2407 McGean-Rohco, Inc. Cleveland, OH 44105-3010
Type II	PENAIR C-5572 NAV-II MA 102-RTU	Penetone Corporation Carlstadt, NJ 07072-2407 ZEP Sales & Service Atlanta, GA 30318-2825 JAD Chemical Co., Inc. San Pedro, CA 90731-1132

TABLE 1. New Qualified Products

via military standard requisitioning systems:

- 6850-01-578-4978 / Type I / Aerosol;
- 6850-01-587-3779 / Type I / Pre-saturated wipes;
- 6850-01-581-9413 / Type II / 32 oz. Trigger Spray; and,
- 6850-01-582-3708 / Type II / 5 Gallon Can.

For additional information on these products, please contact:

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USDA Amends the Guidelines for Designating Bio-based Products for Federal Procurement

By Abdul H. Khalid, Chemical Engineer, HTIS

On July 22, 2011, the United States Department of Agriculture (USDA) announced that the agency was in the process of amending the guidelines for designating bio-based products for Federal Procurement and adding 14 sections to designate items within which bio-based products will be afforded Federal procurement preference. According to the USDA, this program is intended to promote and increase the purchase, as well as use of bio-based products. The following items are designated as bio-based products under Section 9002 of the Farm Security and Rural Investment Act of 2002, and amended by the Food, Conservation, and Energy Act of 2008 (referred to in this document as "section 9002").

- Section, 2902.61- Animal repellents;
- Section, 2902.62- Bath products;
- Section, 2902.63- Bioremediation materials;
- Section, 2902.64- Compost activators and accelerators;
- Section, 2902.65- Concrete and asphalt cleaners;
- Section, 2902.66 - Cuts, burns, and abrasions ointments;
- Section, 2902.67- Dishwashing products;
- Section, 2902.68 -Erosion control materials;
- Section, 2902.69- Floor cleaners and protectors;
- Section, 2902.70- Hair care products;
- Section, 2902.71- Interior paints and coatings;
- Section, 2902.72 -Oven and grill cleaners;
- Section, 2902.73 Slide way lubricants; and,
- Section, 2902.74, Thermal shipping containers.

A bio-based product is defined in Section 9002 as, "A product determined by the Secretary of Agriculture to be a commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant, animal, and marine materials) or forestry materials". Later, the definition of "bio-based product" was revised to include bio-based intermediate ingredients and feedstocks, to make it consistent with certain technical changes to the section 9002 of the Farm Security and Rural Investment Act (FSRIA) as required by the Food Conservation and Energy Act (FCEA) of 2008. Bio-based products must meet the minimum bio-based content under USDA for the applicable product in question to get the "Certified Bio-based Product" label from the agency. In addition, manufacturers provide bio-based content test data or sample data for the bio-based products for an applicable category.

The DoD encourages the Services to increase the use of bio-based products and to minimize the procurement of materials using fossil fuel during the life cycle of the product.

For additional information on this final rule, contact:

- **Ron Buckhalt**
  USDA, Office of Procurement and Property Management
  Washington, DC 20024

  PH: 202.205.4008

  eMail: biopreferred@usda.gov

- Information regarding the Federal bio-based preferred procurement program, one part of the Bio-Preferred Program, is available on the Internet at:

  http://www.biopreferred.gov

Reference:
Federal Register, Vol. 76, No. 141, pages, 43808-43819, July 22, 2011 / Rules and Regulations; and,

Online Ref: http://www.gpo.gov/fdsys/pkg/FR-2011-07-22/pdf/2011-18478.pdf

Occupational Safety & Health News

Tinnitus — a Military Service Related Disability

By Abdul H. Khalid, Chemical Engineer, HTIS

Many American soldiers are exposed to explosive devices that result in traumatic brain injuries. Some complex acoustic traumas such as central auditory process disorders (CAPD), complaints of tinnitus, and non-hearing related complications have been recorded by military audiologists. Hearing damage is one of the leading causes for medical referrals when soldiers return from deployment.

The word tinnitus is derived from the Latin word "tinnire" which means ringing or jingling; a medical condition that involves hearing continuous noise in the ears. Tinnitus, a potentially devastating condition, often reminds many veterans of terrible conditions that they encountered during wars. Tinnitus is not a disease, but it does reflect an abnormality and should be investigated thoroughly. People with hearing loss often complain about tinnitus.

Tinnitus may be caused by high noise exposures, disorders due to certain disease like Lyme disease, head or neck trauma, wax build up, and ototoxicity (some medications). However, the exact physiological cause or causes of tinnitus are still unknown.

Generally, tinnitus is thought to be related to sensorineural hearing loss or occupational loss. Some disturbing facts about tinnitus are:

- Tinnitus is currently the number-one service-connected disability for veterans from all periods of service.
- Since 2005, the number of veterans receiving service-connected disability for tinnitus has increased by at least 15 percent each year.
- The total number of vets awarded disability compensation for tinnitus at the end of 2010 surpassed 744,000.
- At this alarming rate, 2014 will see 1.5 million vets receiving military compensation for tinnitus, at a cost to American taxpayers of over $2.26 billion.

Tinnitus is an inhibition of the brain's auditory circuits due to exposures to blasts, loud music and other unknown causes. Currently, there is no permanent cure. New techniques that image auditory circuits using slices of brain tissue in the laboratory, and drug treatment are being studied, and may one day lead to effective tinnitus treatments.

Often, the use of engineering controls are not feasible, and in such instances only a proper diagnosis, along with an understanding of tinnitus is important. In addition, the proper use and fit testing of hearing protection is important for people with hearing loss because of loud noise exposure, and for those who complain or experience tinnitus. Some suggested tips are:

- If one experiences tinnitus, follow the individualized treatment plans suggested by audiologists, or an ear, nose and throat specialist (ENT) experienced in the treatment of tinnitus.
- Develop good work habits that include protection against noise when working in areas where there is exposure to loud noise. After working in loud noises, select a quiet and calm environment to relax.
- Review your current medications with a medical professional to determine if these medications are possibly contributing to your tinnitus.

For additional information on tinnitus:

Visit website:

http://emedicine.medscape.com/article/856916-overview

Or, contact:

- **Army Institute of Public Health (AIPH)**
  Industrial Hygiene Field Services Program
  ATTN: MCHB-IP-OFS
  5158 Blackhawk Road
  APG, MD 21010

  PH: 410.436.3118 | DSN: 584.3118

  eMail: armyihonline@amedd.army.mil.USAPHC

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6. ATA "At-Risk Population, website at: http://www.ata.org/for-patients/at-risk

Neurotoxicity Due to Chronic Exposure to n-Hexane

By Philip Saunders, Chemical Engineer, HTIS

The chemical n-Hexane (C_6H_{14}, CAS # 110-54-3) exists as a simple straight-chain hydrocarbon molecule (see Figure 1). Physically, n-Hexane is a clear liquid that is most often obtained as a petroleum distillate, and is used in a wide variety of products such as solvents, adhesives, degreasers and various aerosol products. n-Hexane sees wide use as an industrial solvent because it is inexpensive, relatively unreactive and evaporates rapidly. In addition, n-hexane is a minor component of crude oil, and is also a significant component of petroleum products such as gasoline (~10%) and aviation fuel (~2%). It is sometimes referred to as just 'hexane', but the term 'n-hexane' distinguishes the un-branched molecule from the branched forms of hexane that have the same chemical formula. n-Hexane is not generally regarded as a toxic chemical, because short-term, low vapor concentration exposures to it are essentially harmless. However, in sufficient quantities, n-hexane can act as a neurotoxin that targets the nerves in the peripheral nervous system. In 2010, workers at a Chinese electronics manufacturing facility, became severely ill due to the neurotoxic effects of exposure to the n-hexane that they used as a cleaning solvent.

This article provides information on how a seemingly innocuous chemical like n-hexane could have such severe neurotoxic properties due to chronic exposure. In the short term, n-hexane can act as a mild anesthetic, but is otherwise not acutely toxic. On the other hand, chronic exposure to hexane, especially through inhalation of high vapor concentrations, is known to have neurotoxic effects such as loss of coordination, numbness, tingling and cramps in the arms and legs. If the exposure to n-hexane continues, these symptoms may grow progressively worse and can lead to atrophy of the muscles or even the complete loss of muscle function in the arms and legs and eventual paralysis. These effects are not due to an inherent toxicity of hexane itself, but because of how it is metabolized by the liver into another chemical, a diketone called 2,5-hexanedione or hexane-2,5-dione ($C_6H_{10}O_2$, CAS # 110-13-4). See Figure 2 for the structure of this molecule.

Everyone in the general population is occasionally exposed to n-hexane, and can have low levels of 2,5-hexanedione in their blood for short periods and show no ill effects. However, if the exposure to n-hexane is repeated, prolonged or at an elevated concentration, then the liver may convert the n-hexane to 2,5-hexanedione faster than it can be excreted in the urine, and that will cause the 2,5-hexanedione to build up within the body to toxic levels. This is especially true if exposure occurs on a daily basis since it usually takes about 14 hours to reduce the 2,5-hexanedione concentration in the blood by half. This means that once the exposure to n-hexane ends, it will take nearly 4 days for the body to reduce the blood concentration of 2,5-hexanedione to less than 1% of its peak concentration.

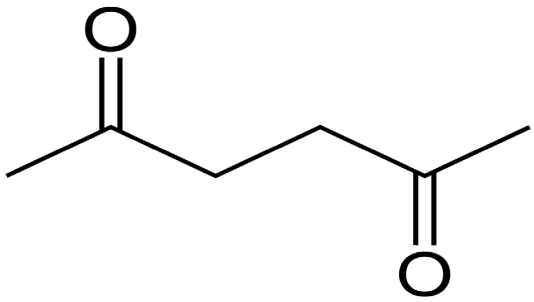
The chemical 2,5-hexanedione acts as a neurotoxin because it targets a specific amino acid within nerve proteins and causes a degradation of the nerve function. The symptoms of chronic overexposure to n-hexane will not be observed or noticed immediately, so it may be difficult to link the symptoms directly to n-hexane without testing for the chemical. On the other hand, the symptoms of n-hexane overexposure may appear, and progress much more rapidly if the exposure occurs in combination with some other organic solvents such as acetone or methyl ethyl ketone.

The symptoms of the neurotoxic effects of 2,5-hexanedione are usually first detected in the feet and toes where sensory nerves are affected and cause the previously mentioned numbness or tingling, but the symptoms can progress beyond that to the point where there is a loss of the ability to stand, walk or grasp objects. The feet and toes are the first to show symptoms because the nerves in the extremities are very long and depend on rapid transmission of the nerve signals, so a loss of nerve function can be particularly noticeable in those areas. The nerve damage that occurs from overexposure to n-hexane is usually not permanent, but recovery may take months or years, and requires the prevention of further exposure.

The illnesses that occurred in China were due to chronic exposure to hexane that was being used as a solvent in the electronics factory, but this could just as easily happen in any workplace environment where workers regularly use aerosol spray paints, solvent cleaners or degreasers. Facilities (and their employees) that regularly use such materials should be aware of the contents of the products that they use by reviewing the material safety data sheet (MSDS), and the warning label applicable to that specific product. If there are significant levels of n-hexane in the products in use, then one may need to consider substitu-

Figure 1

Figure 2



tion of those products with alternatives that do not use that chemical. If that is not a possibility, then respiratory protective equipment may be necessary to prevent overexposures.

A review of recent records entered into the Hazardous Materials Information System (HMIRS) found that most records created during the last year, that have hexane as a chemical component, were for materials in the Federal Supply Class (FSC) 8040 (adhesives). However, that review ignored records that were merely updated and materials that were purchased locally.

In conclusion, this advisory should not be interpreted as meaning that all exposure to n-hexane should be avoided, or that the occasional exposure to it will cause neurological damage since that is not the case. The intention of this article is to raise awareness to the hazards associated with chronic exposure to high concentrations of n-hexane, since awareness to the presence of a workplace hazard is the first step toward protecting against that hazard.

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Other News

Next Generation of Lithium-Ion Batteries Being Developed

By Philip Saunders, Chemical Engineer, HTIS

Rechargeable lithium-ion batteries are becoming more and more prevalent in everyday life. They are used in a multitude of devices such as cell phones, portable computers, and power tools that require an energy-dense rechargeable power source. Electric vehicles also require a rechargeable battery, and lithium-ion batteries are the most likely choice. However, lithium-ion battery technology has not been developed to the point where the durability and energy capacity of these batteries allow completely electric vehicles to be an economical alternative to hybrid or traditional internal combustion vehicles. In a recent press release, scientists at the Lawrence Berkeley National Laboratory announced that they have made a breakthrough that may eventually make electric vehicles, with the resulting lithium-ion batteries, a much more attractive option.

The operational principle behind lithium-ion batteries involves the migration of lithium between its negative electrode and positive electrode. The electrodes are separated by a permeable barrier, and an electrolyte acts as the transfer medium for the ions. As with most batteries, the electrodes act as an anode and cathode, and are connected to each other by a wire that allows electrons to flow between them. During discharge, lithium atoms are ionized at the anode (negative electrode) to create a Li+ ion (cation), plus an electron through an oxidation reaction. The lithium ion then migrates to the cathode (positive electrode) where it undergoes a reduction reaction that adds an electron back to the ion. The flow of electrons from the anode to the cathode creates an electrical current that can be utilized. When the battery is charged, the flow of electrons and lithium ions is reversed by placing a higher voltage on the positive electrode.

For lithium-ion batteries to become an economically viable option for powering vehicles, several technological obstacles must first be overcome. One of the primary obstacles is the energy-to-weight ratio (specific energy or energy density) of the battery. This is important because a high specific energy (often expressed in Watt-hours per kilogram, W h/kg) makes the batteries more efficient to transport by reducing the mass of the battery, and that means a lower consumption of raw materials when manufacturing the batteries. A higher specific energy also allows more stored energy to be carried by a vehicle without increasing the vehicle weight (thus extending its range), or can reduce the energy consumed just moving the mass of the batteries. The specific energy of lithium-ion batteries (150 W h/kg for most common lithium-ion batteries, but as much as 1.5 kW h/kg for cutting edge technology batteries have been reported) is very high when compared to other rechargeable battery chemistries like lead acid (25 W h/kg) or nickel metal hydride (100 W h/kg). However, current lithium-ion battery technology does not yet compare favorably to the 12 kW h/kg energy densities for gasoline or diesel fuel, even when considering the US Department of Energy's estimated energy loss rate of 70% for combustion engines due to heat generation.

Since the battery discharge method depends on electrons obtained from lithium atoms, batteries with more lithium have a higher energy storage capacity. But, increasing the amount of lithium would just make the battery heavier, unless the lithium is stored more efficiently within its cathode and anode, thus increasing the energy density. An inexpensive method to increase the energy density of lithium-ion batteries involves the use of a graphite carbon anode, but that technology has already reached its limit. Within the last few years, a high capacity lithium-ion battery technol-

ogy was developed using an anode made of porous silicon particles that can store lithium much more efficiently than graphite (by a factor of about 10). The silicone particles in the anode are held together by a polymer binder combined with electrically conductive carbon particles. The drawback with this technology is rapid degradation of the battery. This degradation occurs because as the lithium migrates into and out of the silicon particles with each charge/discharge cycle, the silicon particles expand and contract. Repetition of this cycle gradually causes the connections between the carbon particles to break down to the point that the silicone particles become electrically isolated and unable to function. Once the batteries lose enough of their capacity, they must be replaced.

The article from the Lawrence Berkeley National Laboratory announced a breakthrough technology that addresses these two drawbacks. Their method still uses silicon particles to store lithium, but it also uses an electrically conductive polymer binder rather than the polymer and carbon combination that was previously used. This allows the silicon particles to expand and contract without the loss of electrical conductivity seen when using carbon additives in the binder. In addition, since there is no need for the electrically conductive carbon, the silicone particles may be packed much more efficiently than possible with current technologies. This packing is estimated to increase the lithium storage capacity by a factor of eight. The next step in this research will involve developing a cathode with similarly improved durability and storage capacity.

As this new technology is still being developed, there are no batteries on the market that use it. However, these developments may make lithium-ion batteries a much more attractive option for use in electric vehicles, since the batteries will be more durable, and will have either a longer range or a lower weight. As long as their use does not make the country dependent on foreign sources of lithium, they may also be made more attractive should foreign sources of fossil fuels become problematic.

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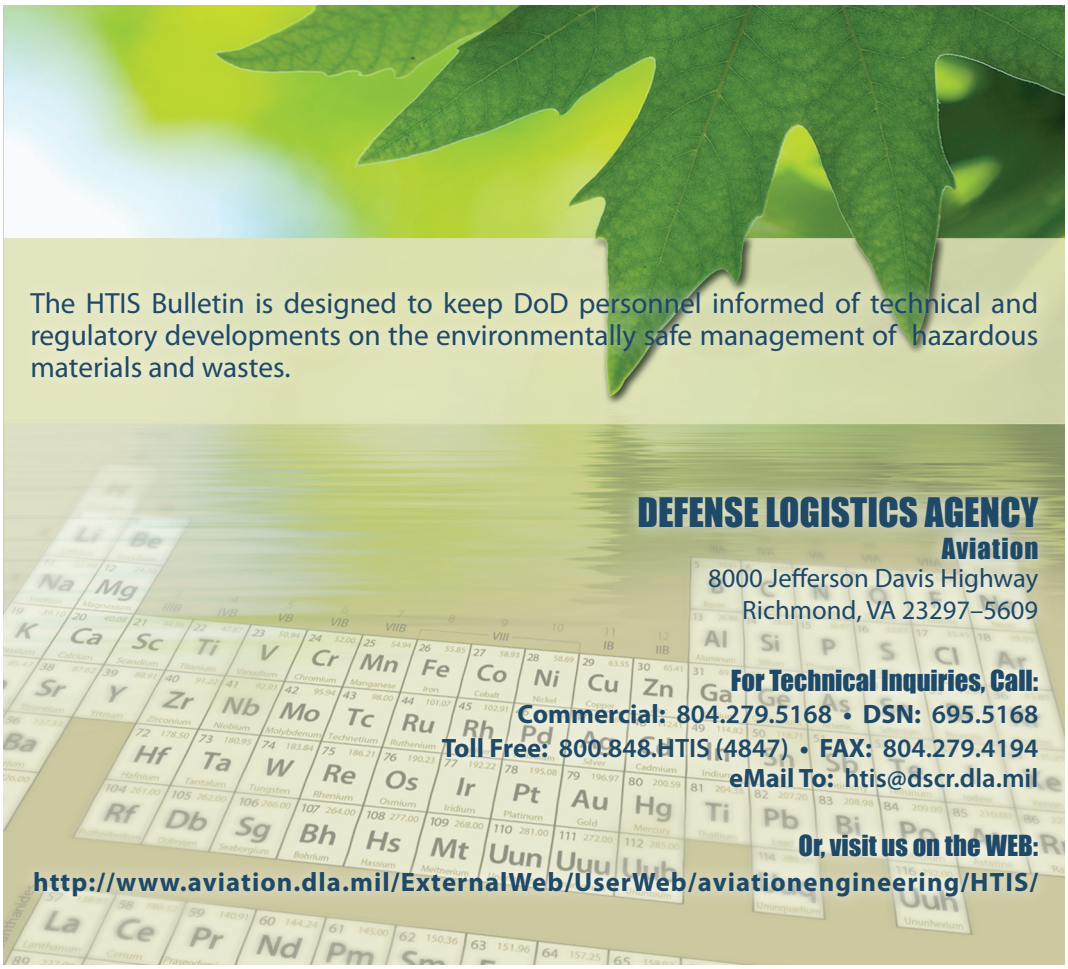
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