# Response to EPA's Hazard Characterization of the Kerosene/Jet Fuel Category The American Petroleum Institute Petroleum HPV Testing Group June 17, 2013

The following comments are in response to EPA's Hazard Characterization (HC) for the Kerosene/Jet Fuel Category (U.S. EPA, 2011). This Category was sponsored by the American Petroleum Institute (API) Petroleum HPV Testing Group (Testing Group) as part of EPA's HPV Chemical Challenge Program (<a href="https://www.petroleumhpv.org">www.petroleumhpv.org</a>).

Below is EPA's generic table of content for all the HPV Hazard Characterizations they have prepared, including Kerosene/Jet Fuel. The Testing Group's comments are found on the page numbers indicated below.

# **Justification for Supporting Chemicals**

Table 1 (HC page 6) has CAS 50815-00-4, JP 4 (heavy kerosene; Fuel No. 1) and CAS 82863-50-1, JP 8 (kerosene; Fuel Oil No. 1) as supporting chemicals. Neither of those CAS numbers are legitimate Chemical Abstract Services (CAS) numbers and they are not on EPA's TSCA Chemical Inventory. JP-4 and JP-8 (aviation turbine fuels for the Department of Defense) are products defined by their military or ASTM specifications. Also, JP-4 is not "heavy kerosene" or "Fuel No. 1" as it contains a significant amount of gasoline range hydrocarbons.

#### 2. General Information on Exposure

The EPA hazard characterization for several Petroleum HPV Categories including Kerosene/Jet Fuel, refers to the category members as complex mixtures when in fact they are Class 2 UVCB substances. (HC page 8 and Tables 2 and 3).

Substances on the US TSCA Inventory are divided into two classes for ease of identification (EPA 1995). Class 1 substances are those single compounds composed of molecules with particular atoms arranged in a definite, known structure. However, many commercial substances that are subject to TSCA are not Class 1 substances, because they have unknown or variable compositions or are composed of a complex combination of different molecules. These are designated Class 2 substances. Class 2 includes substances that have no definite molecular formula representation and either partial structural diagrams or no structural diagrams. These are the "UVCB" substances (Unknown or Variable compositions, Complex reaction products and Biological materials). An example of this kind of substance is given below.

CAS Number: 64742-47-8

CAS Name: Distillates (petroleum), hydrotreated light

<u>CAS Definition</u>: A complex combination of hydrocarbons obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst. It consists of hydrocarbons having carbon numbers predominantly in the range of C9 through C16 and boiling in the range of approximately 150°C to 290°C (302°F to 554°F).

Petroleum substances are subject to nomenclature rules developed jointly by the U.S. EPA and the American Petroleum Institute (EPA, 1995b). In that guidance document, EPA adopts the definitions of petroleum process stream terms provided in API's published reference document Petroleum Stream Terms Included in the Chemical Substance Inventory under TSCA (1983, reprinted in 1985). The Stream Terms definitions include the CAS definition and registry number, the source of the substance and process (i.e., last refining step), short name, indication of carbon number, and indication of distillation range (or other appropriate characteristic). Therefore all members of the Kerosene/Jet Fuel Category are UVCB substances, not mixtures, under EPA's nomenclature guidance.

#### **Genetic Toxicity – in vitro Gene Mutation**

EPA said that the read across conclusion for in vitro gene mutation are "Positive" for untested members of the Kerosene/Jet Fuel Category. (HC Table 4) The Testing Group disagrees and believes the majority of studies support a conclusion of "Negative" for read-across values.

The Testing Group relies on the following evidence;

- 1. A standard Ames assays on two kerosene samples and a sample of Jet A produced negative results with/without activation (API, 1977, 1978, 1979a).
- Optimized Ames assays on four kerosenes also produced negative results (with/without activation) except for one positive assay that occurred with activation (Blackburn, et al., 1986).
- 3. JP-5 (another kerosene-based aviation turbine fuel) was negative in the Ames assay with *Salmonella typhimurium* TA-1535, TA-1537, TA-97, TA-98, and TA-100 at concentrations of 100-10,000  $\mu$ g per plate in the presence or absence of metabolic activation systems from rat or hamster liver (NTP, 1986).
- 4. McKee et al. (1994) evaluated five middle distillate materials, including Jet A, in *Salmonella* strain TA98 and found that they were nonmutagenic; that is, they induced less than a doubling of revertant colonies.

#### **Genetic Toxicity – in vivo Chromosomal Aberrations**

EPA said that the read across conclusion for in vivo chromosome aberrations are "Positive" for untested members of the Kerosene/Jet Fuel Category. (HC Table 4) The Testing Group disagrees and believes the majority of studies support a conclusion of "Negative" for readacross values.

The Testing Group relies on the following evidence;

- Deodorized kerosene (probably a sweetened kerosene, CAS no. 91770-15-9) and Jet A
  produced negative results in dominant lethal assays (API, 1973, 1980b). The deodorized
  kerosene was administered either ip or subcutaneously in rats and mice respectively at 1
  g/kg. The Jet A was administered to mice by inhalation of 100 or 400 ppm for six hours
  a day for eight weeks.
- 2. JP-8 was found to be negative in the dominant lethal assays in both mice and rats at oral doses up to 1.3 mL/kg for 5 days. (Brusick and Matheson, 1978 as cited by NRC, 1996).
- 3. McKee et al. (1994) evaluated five middle distillate materials, including Jet Fuel A, administered by gavage, in the CD-1 mouse bone marrow micronucleus test. No increases in the frequency of MNs were observed for any of the test materials in assessments 24, 48, or 72 hr after treatment. The authors did not see any evidence of bone marrow depression.
- 4. Deodorized kerosene (probably a sweetened kerosene, CAS no. 91770-15-9) and hydrodesulfurized kerosene were negative in in vivo bone marrow cytogenetic tests in Sprague-Dawley rats (API, 1977, 1985d). The test materials had been administered by single ip injection up to 3 g/kg.

#### 4. Hazard to the Environment

The Testing Group disagrees with the approach that EPA used to evaluate the ecotoxicity hazards of the Kerosene/Jet Fuel Category. The endpoint values cited by EPA for read across to all category members were calculated based on measured concentrations of selected hydrocarbons used to verify the presence of hydrocarbons in the water accommodated fractions (WAFs).

In their Hazard Characterization, EPA states that data submitted for the category member, hydrodesulfurized kerosene, were considered inadequate because the results were reported on the basis of nominal loading rates. The Testing Group maintains that toxicity endpoints are more

accurately expressed as 'loading rates' (LL). EPA's HC provides the following statements of findings and effects:

A. Summary (HC page 4 and Data Matrix Table 5, page 31): No adequate data are available for the sponsored substances.

Based on the supporting chemicals, CASRNs 90622-56-3, 64742-48-9, 1120-36-1 and 629-73-2, the 96-h LC50 for fish is 0.11 mg/L, the 48-h EC50 for aquatic invertebrates is 0.9 mg/L and the 72-h EC50 for aquatic plants is 0.4 mg/L for biomass and >0.4 mg/L for growth rate. Based on the supporting chemicals, CASRN 64742-49-0 and 1120-36-1, the 21-d chronic NOEC/LOEC for aquatic invertebrates is 0.17 mg/L and 0.32 mg/L, respectively.

No data gaps were identified under the HPV Challenge Program.

B. Justification for Supporting Chemicals (HC page 5):

For aquatic toxicity, data submitted for the category member, hydrodesulfurized kerosene (petroleum) (CASRN 64742-81-0), were considered inadequate because the results were reported based on nominal loading rates, not measured concentrations. Similarly, data submitted for CASRN 91770-15-9 and 101316-80-7 are not adequate.

EPA's List of supporting chemicals for ecotoxicity (HC page 6):

CAS RN 64742-48-9; Naphtha (petroleum), hydrotreated heavy

CAS RN 64742-49-0; Naphtha (petroleum), hydrotreated light

CAS RN 90300-56-3; Alkanes, C<sub>7-10</sub>, iso-

CAS RN 1120-36-1; 1-tetradecene

CAS RN 629-73-2; 1-hexadecene

The Testing Group believes that results for petroleum UVCBs like Kerosene/Jet Fuel category members (multi-constituent, poorly soluble hydrocarbons) should be expressed as lethal loadings (LL) rather than lethal/effect concentrations (LC, EC). The Testing Group maintains that when toxicity endpoints are more accurately expressed as 'loading rates', substances in the Kerosene/Jet Fuel category are expected to exhibit aquatic toxicity at approximately 1 mg/L or higher for the three trophic levels. Loading is a more effective means of comparing two substances to each other because the hydrocarbon composition in the WAF varies with composition of these streams. Loading is a reflection of the composition and chemistry of the substance and implicitly accounts for dissolution and volatilization of individual hydrocarbon constituents.

Aquatic toxicity of petroleum streams is attributed to the neutral organic hydrocarbon constituents whose toxic mode of action is non-polar narcosis. Hydrocarbons are equitoxic in tissues where the toxic mechanism of short-term toxicity for these chemicals is disruption of biological membrane function (van Wezel and Opperhuizen, 1995). The differences between toxicities (i.e., LC/LL5O, EC/EL50) can be explained by the differences between the target tissue-partitioning behaviors of the individual chemicals (Verbruggen et al., 2000). The existing fish toxicity database for hydrophobic neutral chemicals supports a critical body residue (CBR, the internal concentration that causes mortality) of approximately 2-8 mmol/kg fish (wet weight) (McGrath and Di Toro, 2009). When normalized to lipid content the CBR is approximately 50 µmol/g of lipid for most organisms (Di Toro et al., 2000).

When compared on the basis of standard test methods and exposure solution preparation procedures, kerosene/jet fuel category members are expected to produce a similar range of toxicity for the three trophic level species. Results expressed as measured concentrations of the

fraction of the substance in solution are of little value since it will be virtually impossible to extrapolate to spill situations where the only relevant measures of concentration will be the amount of product spilled and the volume of the receiving environment (i.e., the loading rates). Loading rates provide a unifying concept for expressing the results of a toxicity test with poorly-soluble substances (European Eco-Labeling Criteria; ASTM 2009; GESAMP; OECD 2006; ECHA).

Preparation of independent WAFs based on test substance loading rates is the appropriate procedure for the petroleum UVCB substances in this category because these substances are multi-constituent hydrocarbons whose constituent hydrocarbons vary in water solubility. The dissolution thermodynamics of a multi-constituent hydrocarbon in an aqueous medium limit the likelihood of consistent proportional concentrations of the constituent hydrocarbons at various test substance loading rates. For this reason,

- exposure solutions are not prepared from dilutions of a stock solution (the relative proportion of hydrocarbon constituents in the dilutions would not accurately reflect the relative concentration of those constituent chemicals in individually prepared, successively lower exposure solutions of the test material), and
- separate exposure solutions are prepared at each exposure loading for substances that are multi-constituent hydrocarbons.

Additionally API cannot evaluate the relevancy or reliability of the effects values cited by EPA due to the lack of citations/robust summaries for cited data. In EPA's matrix of SIDS screening data (Table 5, page 31 of the HC), the ecotoxicity values for fish, aquatic invertebrates, aquatic plants, and chronic aquatic invertebrates were derived from data cited in SIDS Initial Assessment Profile (SIAP) of the C7-C9 Aliphatic Hydrocarbons Solvents category. Although the web-site URL's cited in EPA's HC leads one to the SIAP, no details of the studies are provided. The SIDS Initial Assessment Report (SIAR), which may contain study details, has not been completed and not publicly available. EPA provides a one or two sentence summary of the findings, but these cannot allow a determination of the quality of the work, and full robust summaries of the original journal/study reports should be provided.

Further reason to contest values cited by EPA in Table 5, page 31, summary of SIDS data, is that the endpoint values for fish and aquatic invertebrates are all based on unspecified measures of concentration.

#### **Chronic Toxicity to Aquatic Invertebrates**

EPA's review of Testing Group's Test Plan for the Kerosene/Jet Fuel category stated: "The acute toxicity data provided by the submitter for these endpoints are adequate for the purposes of the HPV Challenge Program. EPA suggests that a study of chronic toxicity to aquatic invertebrates be considered for the category member hydrodesulfurized kerosene."

The Testing Group agreed with EPA's conclusions for acute toxicity data and agreed to conduct chronic toxicity testing of hydrodesulfurized kerosene with aquatic invertebrates. Since that time the Testing Group submitted the Category Assessment Document (CAD) using the original dataset for hydrodesulfurized kerosene and two supporting substances that CONCAWE (2001) classifies as kerosene based on similar physical-chemical characteristics (e.g., boiling points distribution and molecular weight range). The Testing Group also has tested hydrodesulfurized kerosene for chronic toxicity to aquatic invertebrates. The Robust Summary for that study is attached to these comments.

# **Appendix**

The composition profiles for the various jet fuels shown in the HC (page 33 and 34) are very misleading. Substances in the Kerosene/Jet Fuel Category have hundreds to thousands of individual hydrocarbon constituents rather than the handful shown in Tables 6, 7, and 8.

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European eco-lubricant labeling criteria:

http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2005:118:0026:0034:EN:PDF

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OECD: Guidance for Testing of difficult substances and mixtures: <a href="http://search.oecd.org/officialdocuments/displaydocumentpdf/?cote=env/jm/mono(2000)6&docla\_nquage=en">http://search.oecd.org/officialdocuments/displaydocumentpdf/?cote=env/jm/mono(2000)6&docla\_nquage=en</a>

Toxic Substances Control Act Inventory Representation for Chemical Substances of Unknown or Variable Composition, Complex Reaction Products and Biological Materials: UVCB Substances (March 29, 1995a); available from <a href="http://www.epa.gov/oppt/newchems/pubs/uvcb.txt">http://www.epa.gov/oppt/newchems/pubs/uvcb.txt</a>

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