

**National Advisory Committee (NAC)
for Acute Exposure Guideline Levels (AEGLs) for Hazardous Substances
Final Meeting 13 Highlights
Wyndham Riverfront Hotel, 701 Convention Center Blvd.
New Orleans, Louisiana 70130
March 11-12, 1999**

INTRODUCTION

George Rusch (NAC Chairman) opened the meeting and welcomed all participants. Attached are the meeting agenda (Attachment 1) and the attendee list (Attachment 2).

The NAC/AEGL Meeting 12 highlights were reviewed and minor changes were requested by John Morawetz and David Belluck. A motion to accept the meeting summary passed unanimously (Appendix A).

STATUS REPORTS AND GENERAL INTEREST ITEMS

National Academy of Sciences (NAS)/Committee on Toxicology (COT)

Roger Garrett (Program Director) stated that the NAS/COT Subcommittee on Acute Exposure Guideline Levels has prepared a preliminary report and was waiting for the completion of the thorough NAS review process. This report addresses the Standing Operating Procedures (SOPs) and eight interim AEGL assessments. A more definitive characterization of hypersusceptible subpopulations and the integration of cancer risk for acute exposures were among the issues the COT identified as topics of concern. He also stated that the SOPs and the five interim assessments will be presented to OECD in response to their interest in the AEGL program.

General Interest Items

- Ceiling Levels
There was discussion regarding the interpretation of AEGLs especially regarding ceiling level terminology (Attachment 3). It was suggested by George Rusch (NAC/AEGL Chairman) that an official definition needed to be established and practical applications of AEGLs needed to be explored.
- Compilation of AEGL-1 Endpoints
Deferred until the next meeting.
- AEGL Dose-Response Family Curves
Ernest Falke gave a brief overview of dose-response data (Attachment 4) for some of the AEGL chemicals and stated that a considerable amount of data were available. This will be an ongoing effort.
- NORA Proposal
Discussion was deferred.

- Children vs. Adults Sensitivity
Bill Pepelko stated that pharmacokinetics may be an important factor regarding variable toxicity between children and adults. Brief discussion ensued regarding the intraspecies uncertainty factor as it pertains to children. The Childrens' Environmental Health Web site (www.cehn.org) was mentioned as a possible source of information.
- Piperidine Reference
Mark McClanahan indicated that the original references in question will be obtained and the findings summarized. (Note: no additional information can be used to expand the current version of TSD).
- Categorical Regression in AEGL Development
Judy Strickland (USEAP/NCEA) presented results of a categorical regression analysis of propylene oxide (Attachment 5). A comparison of this approach to that used by the NAC/AEGL indicated similar determinations of AEGL-1 and AEGL-2 values. AEGL-3 values varied somewhat but not greatly. It was suggested that the results of the categorical regression analysis be incorporated into the appendix section of the propylene oxide Technical Support Document (TSD). Furthermore, Judy offered the results of a categorical regression analysis for methyl isocyanate which had been performed by Dan Guth in 1997. With the application of an uncertainty factor of 6, the results for mild adverse effects, which approximate AEGL-1 values, were comparable to the proposed AEGL-1s.
- IDLH Values and their Relation to AEGLs
Following a statement of the definition of the IDLH (Zarena Post), there was brief discussion regarding the relevance of the IDLH to AEGL levels 2 and 3 (Attachment 6). Richard Niemeier (NIOSH) (absent) would likely be able to provide greater insight into this subject.
- Scientific Judgement in AEGL Development
George Rusch commented on the value of scientific judgement in development of AEGLs. Although graphic presentation of data and modeling techniques are useful, good individual and group judgements are cornerstones of good risk assessment. The NAC/AEGL should continue to rely on the expertise that various members bring to the discussions.
- AEGL Applications
Ernest Falke distributed a draft of the AEGL application write-up (Attachment 3) and requested comments. An attempt to reach consensus on all or part of the draft was deferred. It was suggested that individuals from other agencies/organizations be invited to a future NAC/AEGL meeting to discuss how the AEGLs may be applied.
- Paul Tobin (DFO) indicated that a list of new NAC/AEGL priority chemicals was being drafted and distributed (Attachment 7).

AEGL PRIORITY CHEMICALS

Ethylenediamine, CAS No.107-15-3

Chemical Manager: Mark McClanahan, CDC

Author: Sylvia Milanez, ORNL

Sylvia Milanez provided an overview of data pertinent to developing AEGL values (Attachment 8). There was some discussion regarding the sensitivity characterization (hypersusceptible or not) of individuals sensitized by ethylenediamine. Following discussion regarding the apparently insufficient data relative to AEGL-1, it was decided to address AEGL-2 and AEGL-3 values first. A motion for AEGL-2 by Steven Barbee; seconded by Loren Koller) entailed the use of the NOEL of 59 ppm from a 30-day study in rats exposed for 7 hrs/day, an uncertainty factor of 10 (3 for interspecies and 3 for intraspecies), and using a value of $n=2$ to extrapolate down to 30 min. The proposed values were 30-min, 22 ppm; 1 hr, 16 ppm; 4 hr, 7.8 ppm; and 8 hr, 5.5 ppm. It was noted that this is consistent with the case report of the sensitized human who was exposed as a challenge to ethylenediamine. The values are also consistent with using a 100-fold safety factor with an acute 8-hr study. The motion passed unanimously. A motion was made by Ernest Falke (seconded by Richard Thomas) to develop AEGL-3 values using the same study as used for AEGL-2 (i.e., Pozzani and Carpenter). The determinant for AEGL-3 was the 7-hr, 132-ppm exposure at which there was toxicity seen in only one animal and there was no lethality. This provides a conservative estimate of the lethality threshold and is consistent with the fact that at 225 ppm, the next highest level, there was lethality. Using an n of 2 and a total uncertainty factor of 10 (3 for intraspecies and 3 for interspecies), the resulting AEGL-3 values are: 49 ppm for 30 min, 35 ppm for 1 hr, 17 ppm for 4 hrs, 12 ppm for 8 hrs. The motion passed [YES: 24; NO: 1, ABSTAIN: 0]. A motion was made by Bob Benson (seconded by Ernest Falke) that we do not establish AEGL-1 values for ethylenediamine because there is insufficient data on which to base them. The motion passed [YES: 24; NO: 2; ABSTAIN 0] (Appendix B). John Morawetz indicated that a note should accompany the AEGL values regarding sensitive individuals.

SUMMARY OF REVISED AEGL VALUES FOR ETHYLENEDIAMINE					
Classification	30-min	1-hr	4-hr	8-hr	Endpoint
AEGL-1	ND	ND	ND	ND	Not determined; insufficient data.
AEGL-2	22 ppm 54 mg/m ³	16 ppm 38 mg/m ³	7.8 ppm 19 mg/m ³	5.5 ppm 14 mg/m ³	NOEL for rats exposed 30 days to 59 ppm for 7 hrs/day
AEGL-3	49 ppm 121 mg/m ³	35 ppm 86 mg/m ³	17 ppm 43 mg/m ³	12 ppm 30 mg/m ³	7-hr exposure of rats (toxicity but no deaths) to 132 ppm for 30 days used as a conservative estimate of lethality threshold

Phosphorus trichloride, CAS No. 7719-12-2

Chemical Manager: Tom Hornshaw, Illinois EPA
Author: Robert Young, ORNL

Robert Young provided an overview of the physico-chemical properties and limited toxicity data on phosphorus trichloride (Attachment 9). The deficiencies were especially prevalent regarding exposure-response data for nonlethal endpoints. Draft values for all three AEGL levels were, however, developed to provide strawman reference points as a basis for discussion. Tom Hornshaw presented an overview of several accidental industrial/transport releases of phosphorus trichloride and the responses to these releases. Following discussion regarding the available lethality data, a motion was made by Bob Benson (seconded by Bill Pepelko) that we adopt AEGL-3 values for phosphorous trichloride of 1.6 ppm for 30-min; 1.1 ppm for 1-hr; 0.56 ppm for 4 hr; 0.39 ppm for 8 hr. These are based on a one-third reduction of the 4-hr LC₅₀ in the guinea pig of 50 ppm as an estimate of the non-lethal threshold of 16.7 ppm. These values reflect an uncertainty factor of 10 for interspecies variability, a factor of 3 for intraspecies uncertainty, and a time scaling exponent (*n*) of 2. The motion passed [YES: 18; NO: 8; ABSTAIN 0]. (Appendix C). The motion that we will have insufficient data to derive AEGL-1 and AEGL-2 values and that was made by Dave Belluck and seconded by Kyle Blackman. The motion passed unanimously.

SUMMARY OF PROPOSED AEGL VALUES FOR PHOSPHORUS TRICHLORIDE					
Classification	30-min	1-hr	4-hr	8-hr	Endpoint
AEGL-1	ND	ND	ND	ND	Not determined; insufficient data
AEGL-2	ND	ND	ND	ND	Not determined; insufficient data
AEGL-3	1.6 ppm 8.9 mg/m ³	1.1 ppm 6.2 mg/m ³	0.56 ppm 3.1 mg/m ³	0.39 ppm 2.2 mg/m ³	Estimated lethality threshold based upon 1/3 reduction of guinea pig 4-hr LC ₅₀ (50 ppm/3 = 16.7 ppm).

Phosphorus oxychloride, CAS No. 10025-87-3

Chemical Manager: Tom Hornshaw, Illinois EPA
Author: Robert Young, ORNL

An overview of available data on phosphorus oxychloride was presented by Robert Young (Attachment 10). Quantitative data sufficient for developing AEGL-1 and AEGL-2 values were unavailable and no draft values were presented. Tom Hornshaw also presented information on an accidental release of phosphorus oxychloride (Attachment 11). Lethality data were limited to 4-hr LC₅₀ values in rats and guinea pigs. Draft AEGL-3 values were developed based upon a three-fold reduction of the 4-hr LC₅₀ in rats as an estimated of the lethality threshold (i.e., 48.4 ppm/3 = 16.1 ppm). The draft values were developed using an uncertainty factor of 10 for interspecies variability (no human exposure data and limited animal data in only two species) and an intraspecies uncertainty factor of 3 (mechanism of toxicity appears to be a function of hydrogen chloride and phosphonic acid production resulting in contact irritation and tissue destruction and is not likely to vary among individuals). Due to uncertainties regarding time-dose relationships, the draft values were developed using an *n* of 2 for extrapolation from 4 hrs to 1 hr and to 30 min. and an *n* of 1 for extrapolation

to 8 hrs. However, it was the consensus of the NAC/AEGL that the *n* exponent remain constant at 2. A motion was made Bob Benson (seconded by Bob Snyder) to adopt AEGL-3 values for phosphorus oxychloride of 1.5 ppm for 30-min; 1.1 ppm for 1-hr; 0.54 ppm for 4 hr; and 0.38 ppm for 8 hr based upon the 16.1 lethality threshold estimate, an *n* of 2 and uncertainty factors as described above. The motion passed [YES: 18; NO: 8; ABSTAIN: 0] (Appendix D).

SUMMARY OF PROPOSED AEGL VALUES FOR PHOSPHORUS OXYCHLORIDE					
Classification	30-min	1-hr	4-hr	8-hr	Endpoint
AEGL-1	ND	ND	ND	ND	Not determined; insufficient data
AEGL-2	ND	ND	ND	ND	Not determined; insufficient data
AEGL-3	1.5 ppm 9.4 mg/m ³	1.1 ppm 6.9 mg/m ³	0.54 ppm 3.4 mg/m ³	0.38 ppm 2.4 mg/m ³	Estimated lethality threshold based upon 1/3 reduction of rat 4-hr LC ₅₀ (48 ppm/3 = 16 ppm).

Tetranitromethane, CAS No. 509-14-8

Chemical Manager: Kyle Blackman, FEMA

Author: Sylvia Milanez, ORNL

Sylvia Milanez presented a summary of data relevant to the development of AEGL values for tetranitromethane (Attachment 12). A motion was made by Loren Koller (seconded by Bill Bress/Richard Thomas) that the values as originally proposed for AEGL-1 be adopted. These values were: 30-min, 0.69 ppm; 1 hr, 0.49 ppm, 4 hr, 0.24 ppm, 8 hrs, 0.17 ppm. For AEGL-2: 30-min, 1.7 ppm; 1 hr, 1.2 ppm; 4 hr, 0.61 ppm, and 8 hr, 0.43 ppm. AEGL-3: 30-min, 3.5 ppm ; 1 hr, 2.4 ppm; 4 hr, 1.2 ppm; 8 hr, 0.87 ppm. All of these values are based on the NTP 1990 study. AEGL-1 values are based upon the no-observed-effect threshold of 2 ppm for rats and mice. AEGL-2 values were based upon an exposure level that induced reddening of the lungs in mice (5 ppm). The AEGL-3 values were based upon lethality thresholds in rats and mice (10 ppm). The key study was a 2-week study with a 6-hr/day exposure for 5/days/week. The value for *n* was 2 and it was pointed out that the value of *n* fits both the Kincaid and the Korbakova data. The motion passed (each AEGL level was subject to a separate vote). These votes were AEGL-1 [YES: 21; NO: 5, ABSTAIN 0]; AEGL-2 [YES: 24; NO: 2; ABSTAIN: 0]; AEGL-3 [unanimously] respectively (Appendix E).

SUMMARY OF PROPOSED AEGL VALUES FOR TETRANITROMETHANE					
Classification	30-min	1-hr	4-hr	8-hr	Endpoint

AEGL-1	0.69 ppm 5.6 mg/m ³	0.49 ppm 3.9 mg/m ³	0.24 ppm 2.0 mg/m ³	0.17 ppm 1.4 mg/m ³	Threshold for no observable effects in rats and mice (NTP, 1990)
AEGL-2	1.7 ppm 14 mg/m ³	1.2 ppm 9.8 mg/m ³	0.61 ppm 4.9 mg/m ³	0.43 ppm 3.5 mg/m ³	Pulmonary irritation in mice (NTP, 1990)
AEGL-3	3.5 ppm 28 mg/m ³	2.4 ppm 20 mg/m ³	1.2 ppm 9.8 mg/m ³	0.87 ppm 6.9 mg/m ³	Lethality threshold in mice (NTP, 1990)

Jet Fuels

Chemical Manager: John Hinz, USAF (AL/OEMH)

Author: Sylvia Talmage, ORNL

John Hinz gave a brief overview of jet fuels and delineated the major issues (a complex mixture with variable composition, vapor vs. aerosol exposure, military vs civilian exposure) impacting AEGL development (Attachment 13 and 14). Previous assessments on fuels other than JP-8 and the fact that some of the jet fuels (e.g., JP-4, JP-7) will no longer be used were noted. He emphasized that the AEGL assessment should focus on JP-8. A presentation of current knowledge on various jet fuels was provided by Maj. Les Smith and Maj. Don Christensen, M.D. (Brooks AFB) (Attachment 15). These overviews included characterization of the various jet fuels (application, composition, inventories, etc.) as well as results of USAF worker exposure surveys, and current and future health-related studies (especially on JP-8). Sylvia Talmage then presented a summary of currently available data on JP-4, JP-5, JP-7, and JP-8 (Attachment 16). It was noted that much of the toxicity data are from long-term exposures and that development of AEGL values would be difficult and of uncertain validity, especially for the 30-min, 1-hr, and 4-hr exposure periods. Draft 8-hr AEGL values for all three levels were presented (300 mg/m³, 1700 mg/m³, and 3000 mg/m³, respectively, for AEGL-1, AEGL-2, and AEGL-3). It was the consensus of the NAC/AEGL, however, that the AEGL development for jet fuels be tabled pending availability of information from ongoing and soon-to-be-conducted studies by the USAF.

Sulfur tetrafluoride, CAS No. 7783-60-0

Chemical Manager: Kyle Blackman, FEMA

Author: Carol Forsyth, ORNL

Carol Forsyth reported that the only available information on this chemical was limited to a secondary source and an accident report with no details (Attachment 17). The relevance of sulfuric acid as a decomposition product and the use of hydrogen fluoride as a surrogate were briefly discussed. Because of the lack of chemical-specific data, the uncertainty regarding the breakdown to hydrogen fluoride, and the fact that sulfuric acid has not yet been addressed by the NAC/AEGL, deliberations on sulfur tetrafluoride were deferred indefinitely.

Methyl isocyanate, CAS No. 624-83-9

Chemical Manager: Loren Koller, Oregon State Univ.
Author: Carol Forsyth, ORNL

Carol Forsyth gave a brief summary of available data for methyl isocyanate and presented draft AEGL values (Attachment 18). Judy Strickland stated that categorical regression analysis provided 30-min and 1-hr AEGL values that were lower (analysis not provided). A discussion on the mechanism of action of methyl isocyanate focused on the irritation and possible developmental effects as inferred by spontaneous abortion rates in the Bhopal incident. A motion to accept the following AEGL-3 values was made by Bob Benson (seconded by Ernest Falke): 0.4 ppm for 30 min; 0.2 ppm for 1 hr; 0.05 ppm for 4 hrs; 0.025 ppm for 8 hrs. These values were based upon an increased number of deaths in rat pups born from mothers who were exposed to 3 ppm during gestation. At 1 ppm there was no increase in death of pups compared to the controls. An *n* of 1 for time scaling is based upon an extrapolation of lethality data. An uncertainty factor of 3 for interspecies variability was applied because there was agreement between two species and two separate laboratory reports. An uncertainty factor of 10 was applied for intraspecies variability because of uncertainties regarding the mechanism of action. The motion passed unanimously (Appendix F). Further deliberations were tabled due to lack of time.

SUMMARY OF PROPOSED AEGL VALUES FOR METHYL ISOCYANATE					
Classification	30-min	1-hr	4-hr	8-hr	Endpoint
AEGL-1*					
AEGL-2*					
AEGL-3	0.4 ppm 0.95 mg/m ³	0.2 ppm 0.42 mg/m ³	0.05 ppm 0.12 mg/m ³	0.025 ppm 0.06 mg/m ³	Neonate lethality in rats following gestational exposure of dams to 3 ppm (Schwetz et al., 1987)

*To be determined at next meeting

ADMINISTRATIVE ISSUES

Future meetings

The following meeting dates and locations have been proposed:

June 14-16, 1999 (Washington, D.C.)
September 14-16, 1999 (Rutgers University, N.J.)
December 6-8, 1999 (Washington, D.C.)

These highlights were prepared by Robert Young and Po-Yung Lu, ORNL.

LIST OF ATTACHMENTS

The attachments were distributed during the meeting and will be filed in the EPA Docket Office.

1. NAC/AEGL Meeting No. 13 Agenda
2. NAC/AEGL Meeting No. 13 Attendee List
3. Draft of AEGL Application Write-up - Ernest Falke
4. Dose- response family curve - Ernest Falke
5. Categorical Regression Analysis of Propylene Oxide - Judy Strickland
6. Definition of IDLH - Zarena Post
7. Second list of draft NAC/AEGL priority chemicals - Paul Tobin
8. Data Analysis of Ethylenediamine - Sylvia Milanez
9. Data Analysis of Phosphorus trichloride - Robert Young
10. Data Analysis of Phosphorus oxychloride - Robert Young
11. Accidental Release Data of Phosphorus oxychloride - Tom Hornshaw
12. Data Analysis on Tetranitromethane - Sylvia Milanez
13. Overview of Jet Fuels - John Hinz
14. Factors impacting the development of AEGLs of Jet Fuels - John Hinz
15. Current Knowledge on Jet Fuels - Les Smith and Don Christiansen
16. Data Analysis of JP-4, JP5- JP-7, and JP-8 - Sylvia Talmage
17. Data Analysis of Sulfur Tetrafluoride - Carol Forsyth
18. Data Analysis of Methyl Isocyanate - Carol Forsyth

LIST OF APPENDICES

- A. Approved NAC-AEGL-12 Meeting Highlights
- B. Ballot for Ethylenediamine
- C. Ballot for Phosphorus trichloride
- D. Ballot for Phosphorus oxychloride
- E. Ballot for Tetranitromethane
- F. Ballot for Methyl isocyanate

**National Advisory Committee for
Acute Exposure Guideline Levels for Hazardous Substances**

NAC/AEGL-13

Wyndham Riverfront Hotel
701 Convention Center Blvd., New Orleans, LA 70130
Phone: 504-524-8200

AGENDA

Thursday, March 11, 1999

8:00 - 8:15 AM Introductory remarks and approval of NAC/AEGL-12
Highlights (George Rusch, Roger Garrett, and Paul Tobin)

8:15 - 10:15 **STATUS REPORTS**

- Definition of "ceiling" values for SOP - 10 min.
(Ernie Falke)
- Compilation of AEGL-1 endpoints - 10 min. (Ernie Falke)
- AEGL Dose-response family curves - 15 min. (Ernie Falke)
- Report on NAS/COT-AEGL Subcommittee - 10 min.
(Roger Garrett)
- NORA proposal -10 min. (Paul Tobin and Richard Niemeier)
- Sensitivity of Adults vs Children - 10 min.
(Bill Pepelko)
- Reference clarification - Piperidine - 5 min.
(Mark McClanahan)
- Scientific judgement of AEGL development - 15 min.
(George Rusch)
- Comparison of toxicity values derived by ARE vs AEGL
approaches - 30 min. (Judy Strickland)
- Purpose of IDLHs and Relevance to AEGLs - 10 min.
(Zarena Post, Richard Niemeier)

10:15 - 10:30 **Break**

10:30 - 12:00 Ethylenediamine (Mark McClanahan/Sylvia Milanez)

12:00 - 1:00 PM **Lunch**

1:00 - 2:15 Phosphorus oxychloride (Tom Hornshaw/Robert Young)

2:15 - 2:30 **Break**

2:30 - 3:45 Phosphorus trichloride (Tom Hornshaw/Robert Young)

3:45 - 5:00 Tetranitromethane (Kyle Blackman/Sylvia Milanez)

5:00 - 5:15 Administrative issues, future meetings

Friday, March 12, 1999

8:00 - 8:30 AM Tetranitromethane (continued)

8:30 - 10:30 Jet Fuel (JP-4, -5, -7, & -8) (John Hinz, Glenn Leach,
Ken Still/Sylvia Talmage)

10:30 - 10:45 **Break**

10:45 - 12:00 Methyl isocyanate (Loren Koller/Carol Forsyth)

12:00 - 1:00 PM **Lunch**

1:00 - 2:00 Methyl isocyanate (continued)

2:00 - 2:15 **Break**

2:15 - 3:00 Sulfur tetrafluoride (Kyle Blackman/Carol Forsyth)

3:00 Adjourn

NAC/AEGL-13

Attachment 2

3/1-12/99

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NAC/AEGL-13

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Kyle Blackman	FEMA	202-646-4676
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Sudy Strickland	EPA/ORD/NCEA	919 541 4930

Characterization, Interpretation and Proper Application of the Acute Exposure Guidance Levels (AEGLs)

AEGL values are developed as threshold concentrations of acutely toxic chemicals in air that are predicted to elicit a specific adverse health effect following exposure for a specified period of time. The AEGL values developed by the NAC/AEGL Committee are ceiling exposure values and are not intended to accommodate even temporary excursions in airborne concentrations above the established AEGL levels. Consequently, the AEGL values cannot, and should not, be considered as “time weighted averages” that may be derived from various concentrations above and below the published AEGL value over the span of the specified exposure period. For example, the thirty (30) minute AEGL-2 value for a given chemical cannot be exceeded at any time during the specified exposure period without the likelihood of eliciting a more adverse health effect than that defined for the particular AEGL-2 level in question, even though the “time weighted average” for the total thirty-minute period may be below the established AEGL-2 level. This same example applies to all AEGL levels at all specified exposure levels .

Further, each individual AEGL value and its corresponding exposure period represents a discrete dose-response threshold in humans for a defined adverse health effect based on a one-time, episodic exposure at the specified concentration and exposure period. Therefore, the AEGL values established are not intended to apply to subsequent exposures to the chemical at the same AEGL level or any other AEGL level, irrespective of whether the subsequent airborne concentrations are higher or lower and the exposures are intermittent or continuous. For example, the AEGL-2 value for 30 minutes was not established with the consideration that additional exposures to the same chemical may occur in the future. This same example applies to all AEGL levels at all specified exposure levels.

The NAC/AEGL Committee is developing AEGL levels for at least 4 different exposure periods (0.5, 1, 4, and 8 hours), and in certain cases, for 10 minutes. This wide range of exposure periods is intended to provide insight and flexibility for chemical emergency planning, response, and prevention by agencies and organizations in both the public and private sectors. However, in certain instances, there may be a critical need for one or more AEGL values at exposure periods other than those developed by the NAC/AEGL Committee.

Although it is possible to develop AEGL values for additional exposure periods, it is important to emphasize that such values should be developed only for exposure periods that lie between any two AEGL values developed by the NAC/AEGL Committee. Further, the AEGL values developed for one or more additional exposure periods are valid only if the methodologies used by the NAC/AEGL Committee are rigorously adhered to. The equation $C^n \times t = k$ (ten Berge, et al, 1986) is used to express the relationship between the airborne concentration (C) and the exposure period (t). The desired AEGL value for an unpublished exposure period can be determined by employing the same value of n in the equation $C^n \times t = k$ that was used by the Committee to time-scale the two established AEGL values located adjacent to the unpublished exposure period of interest. In instances where it is not possible, or not desired, to calculate an

AEGL value for an unpublished exposure period employing the Committee's methodology, the published AEGL value for the longest published exposure period that most closely matches the exposure duration of interest should be used.

Estimates of ceiling exposure values for time periods that are less than the shortest duration for which the NAC/AEGL Committee has developed an AEGL value, should not exceed this established value, irrespective of the length of the exposure period in question. For example, a ceiling value to be selected for a 10-minute exposure period should not exceed the corresponding 30-minute AEGL value if the latter represents the shortest exposure period for which the NAC/AEGL Committee has established an AEGL value.

P value	5		
C at P value	50.1		
m value	5.7		
Desired P level	4		
b =	-4.68908	P value	Response
C at desired P level	33.45023	4	
C at P = 5	50.1	5	0.5
C at P = 4	33.45023	4	0.32
C at P = 3	22.33369	3	0.05
C at P = 2	14.91152	2	0.01
C at P = 1	9.955965	1	

COMPUTING CONCENTRATIONS FOR DIFFERENT P VALUES

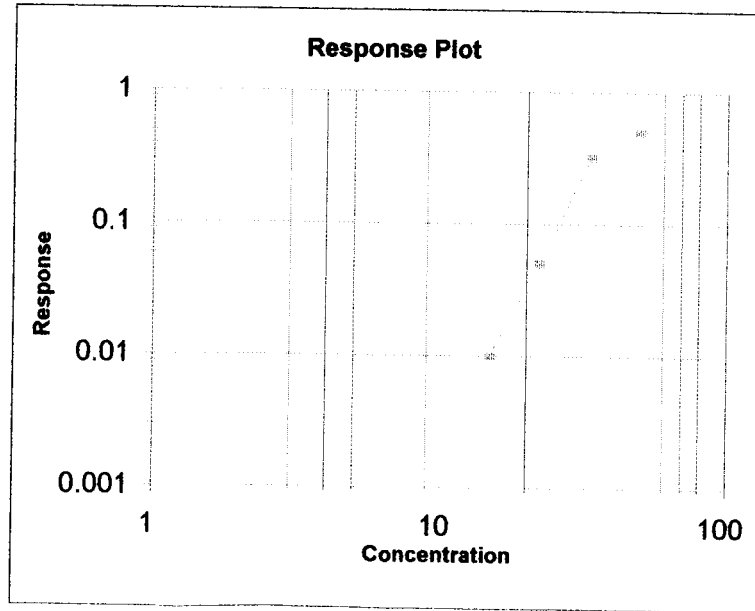
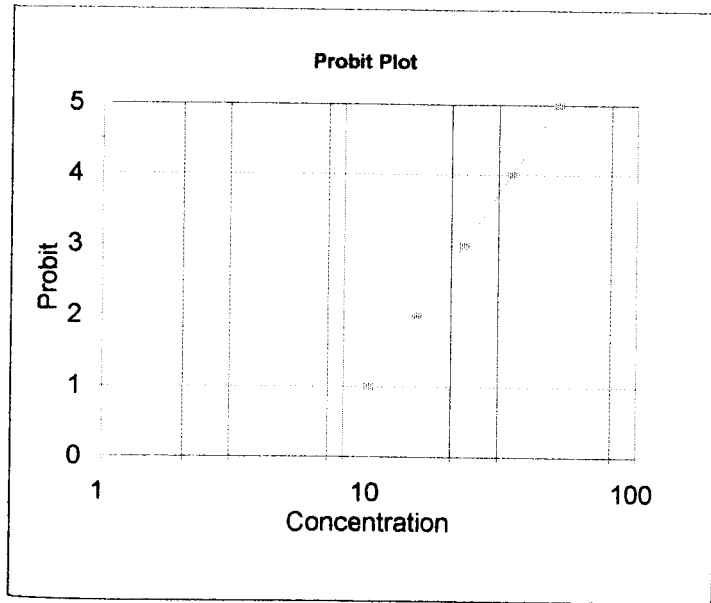
P = P value
 C = Concentration
 m = slope = $\Delta P / \Delta \text{LOG}(C)$
 b = y intercept

(Eqn 1) $P = m(\text{LOG}(C)) + b$

(Eqn 2) $b = P - m(\text{LOG}(C)) + b$

(Eqn 3) $\text{LOG}(C) = (P - b)/m$

(Eqn 4) $C = 10^{(P - b)/m}$



Categorical Regression Analysis of Propylene Oxide

Judy A. Strickland
National Center for Environmental Assessment
U.S. Environmental Protection Agency

National Center for Environmental Assessment



Categorical Regression

- Group effect data into severity categories
 - No adverse (0)
 - Adverse (1)
 - Lethal (2)
- Calculate probability-response (severity) relationship for concentration and duration
- 10% probability \geq Adverse effects = 90% probability No observed adverse effects

2

CatReg Model

$$\Pr(Y \geq s | C, T) = H(\alpha_s + \beta_1 C + \beta_2 T)$$

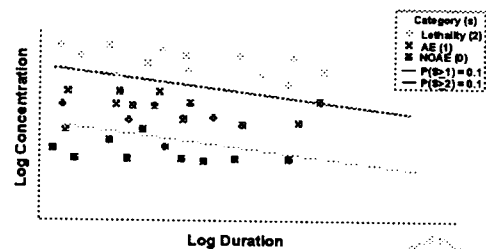
s = Response as severity category
0, No observed adverse effect
1, Adverse effect
2, Lethal effect

C = Concentration
T = Exposure duration

National Center for Environmental Assessment



Categorical Regression Schematic



National Center for Environmental Assessment



Data Set

- CMA, 1998
- Dow, 1981
- Jacobson et al., 1956
- Rowe et al., 1956
- Shell Oil Co., 1977
- NTP, 1985

5

Types of Data

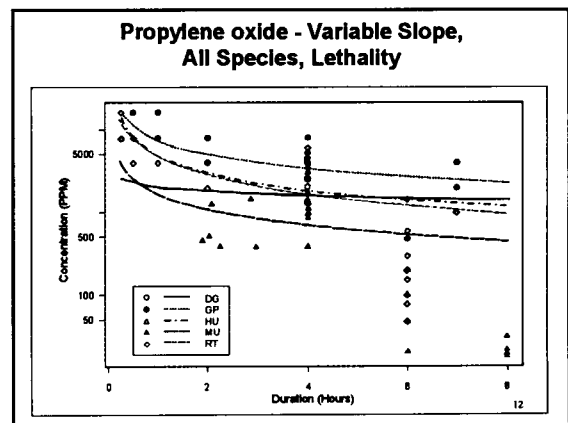
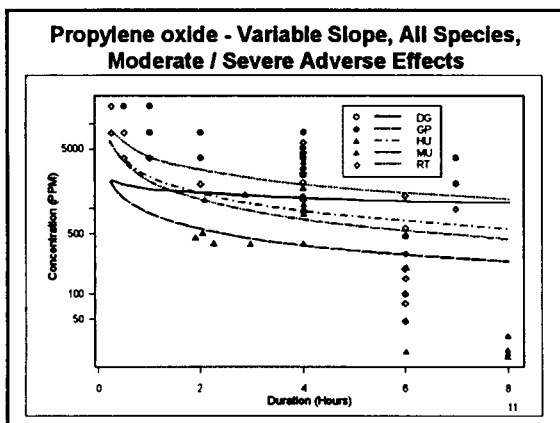
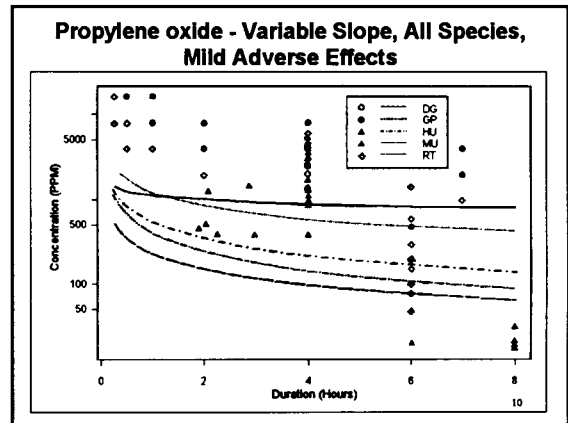
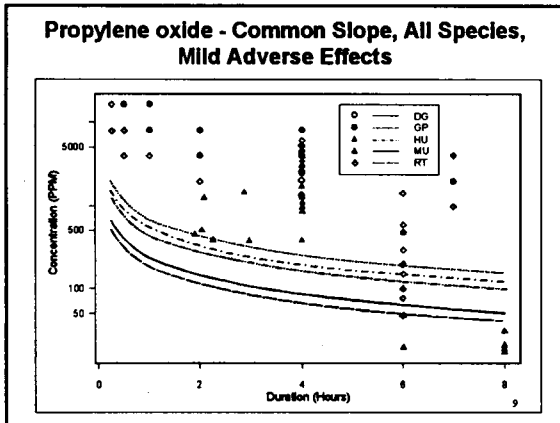
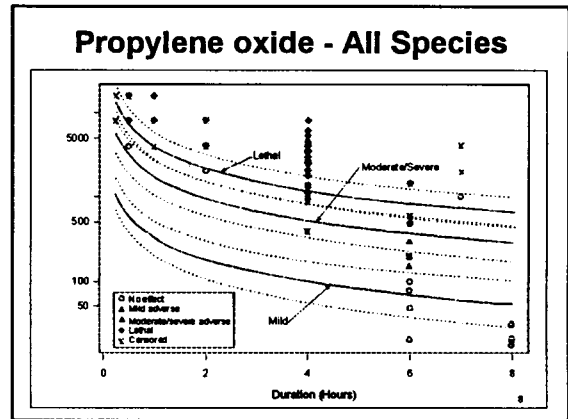
- 6 Studies, 139 data points
- Humans, rats, mice, dogs, guinea pigs
- Irritation—eyes, nose
- Clinical signs—dyspnea, restlessness, piloerection, salivation, vomiting,
- Death
- 15 min - 8 h
- Incidence

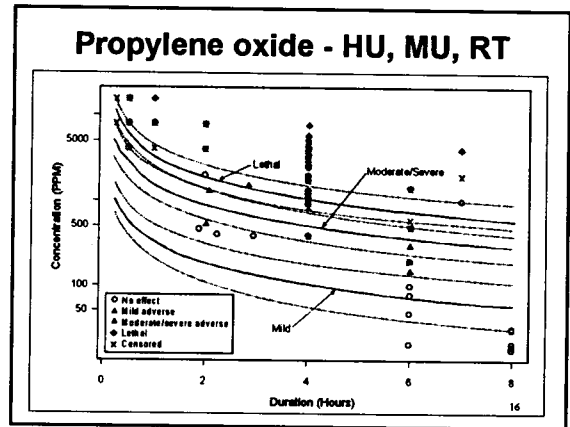
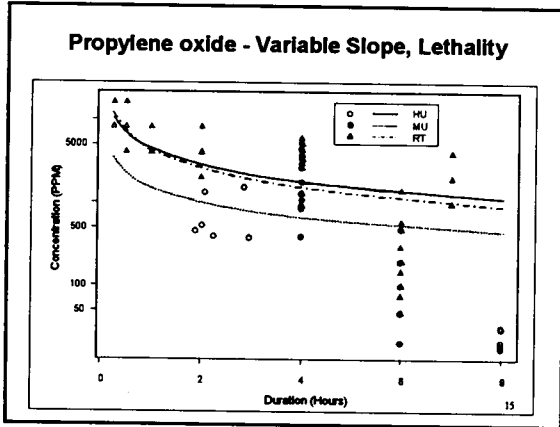
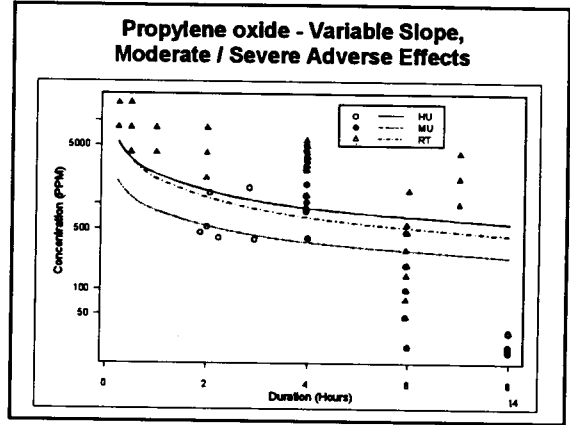
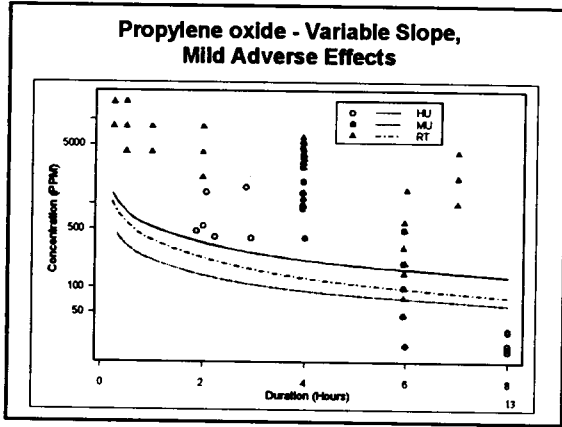
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Severity Categories

- No-observed-adverse effect
- Mild adverse effect
- Moderate/severe adverse effect
- Lethal effect
- Censored data

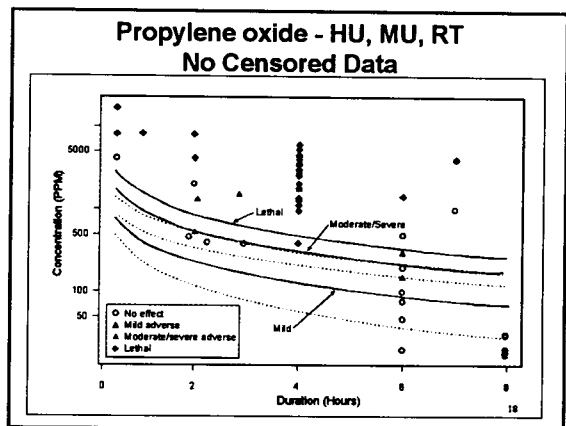
7





Categorical Regression Results

Severity	Duration (h)	EC-T10	95% LCL
1	0.5	580	375
1	1	325	200
1	4	100	55
1	8	55	30
2	0.5	2900	1875
2	1	1625	1075
2	4	500	325
2	8	280	175
3	0.5	6200	4600
3	1	3400	2550
3	4	1050	725
3	8	600	400



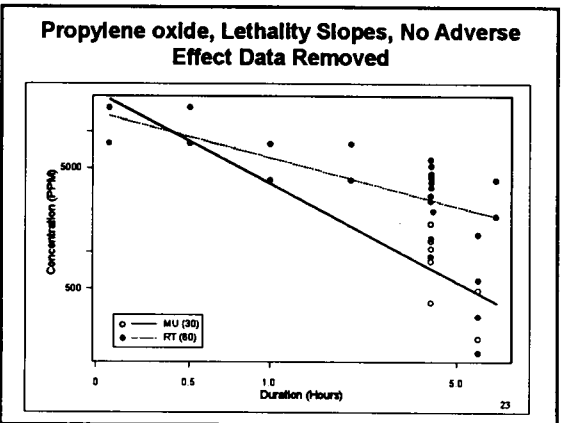
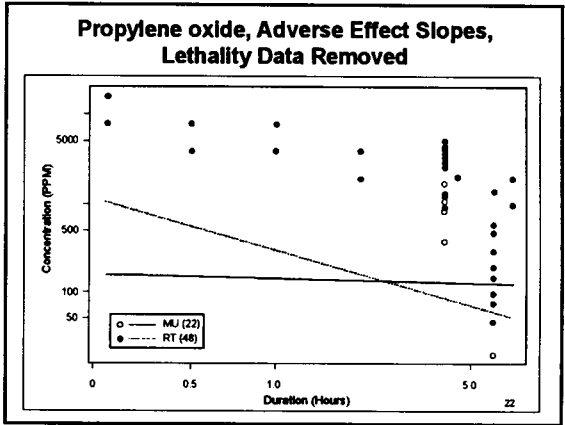
Categorical Regression Results without Censored Data

Severity	Duration (h)	EC10	95% LCL
1	0.5	745	460
1	1	405	235
1	4	125	60
1	8	70	30
2	0.5	1730	860
2	1	970	540
2	4	290	200
2	8	160	110
3	0.5	2600	1325
3	1	1440	810
3	4	440	280
3	8	240	150

Comparison of Categorical Regression Values to AEGLs

Exposure Duration	Severity1 (ppm)	AEGL-1 (ppm)	Severity2 (ppm)	AEGL-2 (ppm)	Severity3 (ppm)	AEGL-3 (ppm)
30 min	375	110	1875	510	4600	1100
1 h	200	60	1075	290	2550	610
4 h	55	19	325	91	725	190
8 h	30	11	175	51	400	110

- ### Slope Analysis for Adverse vs Lethal Effects
- To identify slopes/n's
 - No-observed-adverse effect + Adverse effect
 - Calculate 10% Probability Adverse Effects
 - Adverse effect + Lethal effect
 - Calculate 10% Probability Lethal Effects



Slopes for Adverse & Lethal Effects

	Rats & Mice	Rats	Mice
Adverse Slope	-0.75	-0.89	-0.07
n	1.3	1.1	15
Lethality Slope	-0.75	-0.58	-1.2
n	1.3	1.7	0.9

3/10/99

**Duration Extrapolations
with Various n's**

n	1hr	8 hr
1.1	200 ppm	30 ppm
1.7	200 ppm	59 ppm

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Purpose of establishing an IDLH

to "ensure that the worker can escape
from a given contaminated environment
in the event of failure of the respiratory protection equipment."

Established as a matter of NIOSH policy, as part of the respirator
selection process.

<http://www.cdc.gov/niosh/idlh/idlhintr.html>

Definition of IDLHs

Immediately Dangerous to Life or Health condition:

a situation

"that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment."

<http://www.cdc.gov/niosh/idlh/idlhintr.html>

AEGL-3 Definition

AEGL-3 is the airborne concentration ... above which it is predicted that the general population, including "susceptible" but excluding "hypersusceptible" individuals,

could experience life-threatening effects or death.

Airborne concentrations below AEGL-3 but at or above AEGL-2 represent exposure levels which

may cause irreversible or other serious, long-lasting effects or impaired ability to escape.

IDLH/AEGL Considerations

How do the definitions of IDLHs and AEGLs compare?

What populations are IDLHs and AEGLs set to protect?

If there are no errors in the derivation of the IDLH, where does the IDLH “fit” in the AEGL spectrum?

Note: NIOSH is comparing IDLHs and AEGLs and considering whether they need to continue authoring IDLH values.



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

February 17, 1999

Dear Committee Member:

Attached please find the Second Priority List for Acute Exposure Guideline Level development. I have assembled this list in the same manner that was used for the first priority list of 85 chemicals, by combining chemicals from lists that have been submitted to me by member federal agencies.

Please let me have your comments on this list by March 5, 1999.

Sincerely,

Paul S. Tobin

Paul S. Tobin, Designated Federal Officer
NAC/AEGL Committee

OPTIONAL FORM 99 (7-90)

FAX TRANSMITTAL # of pages **2**

To Po-Yung Lu	From Paul Tobin
Dept./Agency 423 241-0399	Phone 260-1736
Fax #	Fax #

NSN 7540-01-317-7368 5099-101 GENERAL SERVICES ADMINISTRATION

Second List of 50 Priority Chemicals for Acute Exposure Guideline Level (AEGL) Development*

Contact: Paul S. Tobin, Ph.D. (202) 260-1736 e-mail tobin.paul@epa.gov

February 17, 1999

ORGANIZATION LISTS

¹ATSDR Medical Management

Agency for Toxic Substances and Disease Registry

X+ = ATSDR "Top 20" Toxicology Profile Chemicals

X = Chemicals with an ATSDR Toxicology Profile

²DOD

Department of Defense

X = On one or more lists as follows:

Army Toxicity Summary Chemical

Chemical Weapons Convention Schedule 3.A Toxic Chemical

Chemical Stockpile Emergency Preparedness Program (CSEPP) Chemical

Air Force Installation Restoration Program Chemical

Navy Chemical

Strategic Environmental Research and Development Program (SERDP) Chemical

³DOE SCAPA

DOE Subcommittee for Consequence Assessment and Protective Action Chemical

⁴DOT ERP

Department of Transportation Emergency Response Guidebook

⁵EPA CAA 112b

Environmental Protection Agency Clean Air Act 112b Chemical

⁶EPA CAA 112r

Environmental Protection Agency Clean Air Act 112 Chemical

⁷EPA Superfund

Environmental Protection Agency Superfund Chemical

⁸OSHA PSM

OSHA Process Safety Management Chemical

⁹Seveso Annex III

International Seveso Convention List

¹⁰NIOSH IDLH

National Institute for Occupational Safety and Health Immediately Dangerous to Life or Health

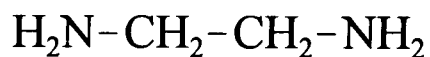
* This second list of 51 priority chemicals adds to the initial list of 85 priority chemicals for AEGL development. This list, shown below, has been created by merging priority hazardous chemical lists of various organizations. This list provides chemicals for AEGL development by the National Advisory Committee for Acute Exposure Guideline Levels for Hazardous Chemicals (NAC/AEGL). However, the list of chemicals is susceptible to modification, pending further input from the organizations that make up the NAC/AEGL. While it is anticipated that most of these chemicals will remain of high priority for AEGL development, changes to the list could occur.

Any one organization list should not be interpreted as being of interest only to that organization in whose list the chemical appears. Certain lists, such as the EPA CAA 112r list, are considered important to organizations other than EPA, since any facility and site that possesses these chemicals are responsible for federal regulatory requirements triggered by the listed chemicals. In addition, many of the hazardous chemicals listed below are commodity chemicals, the AEGLs for which are of potential importance to many organization programs.

CAS NO.	CHEMICAL	¹ ATSDR	² DOD	³ DOE SCAPA	⁴ DOT ERG	⁵ EPA CAA 112b	⁶ EPA CAA 112r	⁷ EPA Super fund	⁸ OSHA PSM	Seveso Annex III	⁹ IDLH
50-00-0 ✓	Formaldehyde	X					X		X	X	X
64-18-6	Formic acid			X							
67-64-1 ✓	Acetone	X	X	X							
71-55-6 ✓	1,1,1-Trichloroethylene	X	X	X		X		X			
74-83-9 ✓	Methyl bromide	X			X	X		X	X	X	X
74-87-3 ✓	Methyl chloride	X				X	X	X	X		X
74-88-4 ✓	Methyl iodide				X				X		X
75-00-3	Chloroethane	X	X	X							
75-01-4	Vinyl chloride	X+	X			X		X			
75-07-0	Acetaldehyde					X			X		X
75-15-0 ✓	Carbon disulfide					X	X			X	
75-25-2	Bromoform		X								
75-35-4 ✓	1,1-Dichloroethylene	X	X	X				X			
75-45-6	Chlorodifluoromethane (Freon)			X							
75-63-8	Trifluorobromomethane (Halon 1301)			X							
75-71-8	Dichlorodifluoromethane		X	X							
76-06-2	Chloropicrin		X		X				X		X
77-78-1	Dimethyl sulfate						X				
78-93-3	Methyl ethyl ketone		X				X				

CAS NO.	CHEMICAL	¹ ATSDR	² DOD	³ DOE SCAPA	⁴ DOT ERG	⁵ EPA CAA 112b	⁶ EPA CAA 112r	⁷ EPA Super fund	⁸ OSHA PSM	Seveso Annex III	⁹ NIOSH IDLH
79-11-8	Chloroacetic acid						X				
95-63-6	Trimethyl benzene		X	X							
97-02-9	2,4-Dinitroaniline			X					X		
100-41-4	✓ Ethyl benzene	X	X	X							X
100-42-5	Styrene	X				X					X
100-44-7	Benzyl chloride					X					X
107-06-2	1,2-Dichloroethane		X					X			X
107-13-1	✓ Acrylonitrile	X				X	X			X	X
108-05-4	Vinyl acetate monomer	X					X				X
108-90-7	Chlorobenzene	X	X								X
108-95-2	Phenol	X	X			X					X
109-99-9	Tetrahydrofuran			X							X
110-86-1	Pyridine	X		X							X
111-36-4	n-Butyl isocyanate				X						X
141-78-7	Ethyl acetate			X							X
144-62-7	Oxalic acid			X							X
463-58-1	Carbonyl sulfide				X						
542-88-1	Chloromethyl ether						X			X	
556-64-9	Methyl thiocyanate						X				
630-08-0	Carbon monoxide				X						X
674-82-8	Diketene				X						

**ACUTE EXPOSURE GUIDELINE LEVELS (AEGLs)
FOR
ETHYLENEDIAMINE**



March 11-12, 1999

ORNL Staff Scientist: Sylvia Milanez
Chemical Manager: Mark McClanahan
Chemical Reviewers: Loren Koller, Richard Thomas

INTRODUCTION

- ▶ Ethylenediamine (EDA) is a very basic, hygroscopic, flammable liquid used to stabilize rubber latex, in antifreeze solutions, in the preparation of dyes, resins, insecticides, etc. (HSDB, 1999).
- ▶ EDA is a high production volume chemical: 64 million lbs. in U.S. in 1985. Current U.S. producers: Dow Chemical Co., Union Carbide Corp., RSA Corp. (USITC, 1995; HSDB, 1999).
- ▶ EDA is an eye, mucous membrane, and respiratory irritant and a well-known respiratory and skin sensitizer. Respiratory sensitization reported from exposure to < 1 ppm EDA (Aldrich, 1987).
- ▶ Both *immediate* and *delayed* (few hours) asthmatic responses reported (rhinitis, coughing, wheezing, shortness of breath, bronchospasm).
- ▶ EDA inhalation caused hair loss and lung, kidney, and liver damage in rat and guinea pig studies.
- ▶ Mechanism of EDA toxicity or respiratory sensitization is unknown. EDA is water and lipid-soluble and can penetrate cells and cause delayed damage and cell death. Edema can follow.

Data Relevant to AEGL-1

- ▶ *No appropriate human studies* (exposure too short or not defined).
- ▶ Rats (15/sex) exposed to 59 ppm EDA 7 hrs/day for 30 days had no toxic effects (Pozzani and Carpenter, 1954); use single exposure for derivation.

Rat (Pozzani & Carpenter, 1954)	7 hrs/day for up to 30 days	59	▶ no effects noted
		132	▶ hair loss; more (undefined) microscopic lesions (0/26 toxic deaths, 4 die of infection)
		225	▶ 16/20 toxic deaths (mean 17.4 days); liver, kidney effects; hair loss (10 die of infection)
		484	▶ 30/30 toxic deaths (mean 11.4 days); liver, kidney, lung, adrenal effects; hair loss

AEGL-1

Key study: Pozzani and Carpenter, 1954

Toxicity endpoint: NOAEL in Sherman rats (15/sex) exposed 7 hrs/day for 30 days to 59 ppm EDA. Use single exposure for derivation.

Scaling: $C^2 \times t = k$ ($n = 2$; ten Berge et al., 1986)
 $(59 \text{ ppm})^2 (7 \text{ hrs}) = k = 24367 \text{ ppm-hrs}$

Total uncertainty/modifying factor: 20

Uncertainty factor: 10

Intraspecies: 3 - response to irritant gas not likely to vary greatly among humans

Interspecies: 3 - although based on only one species, 10 was not used because study was multiple-exposure and no adverse effects were noted

Modifying factor: 2 - very limited overall database

TABLE 4. AEGL-1 Values for Ethylenediamine [mg/m ³]			
30 minutes	1 hour	4 hours	8 hours
11 ppm [27]	7.8 ppm [19]	3.9 ppm [9.6]	2.8 [6.8]

NOTE THAT hypersusceptible individuals, i.e. sensitized to EDA, may experience effects beyond the scope of AEGL-1.

Data Relevant to AEGL-2

- ▶ *No appropriate human studies.* Bronchial provocation test (30 ppm EDA for 15 min.) on EDA-sensitized (“hypersusceptible”) worker not used by NAC/AEGL.
- ▶ Rats and guinea pigs exposed for 8 hrs to ~484 ppm (1000 ppm nominal) all survived 2 weeks, and had “light cloudy swelling of the kidney” and bronchiolar edema of unspecified severity (Carpenter et al., 1948).
- ▶ Rat 30 exposure (7 hrs/day) study (Pozzani and Carpenter, 1954) in which 225 or 484 ppm caused hair loss, kidney, liver, lung toxicity, and **death** starting on day 3 (484 ppm) or 4 (225 ppm). Can’t use because toxicity from 1 exposure is unknown.

AEGL-2

Key study: Carpenter et al., 1948

Toxicity endpoint: Bronchiolar edema; cloudy swelling of kidneys in rats and guinea pigs exposed for 8 hrs to ~484 ppm (1000 ppm nominal)

Scaling: $C^2 \times t = k$ ($n = 2$; ten Berge et al., 1986)
 $(484 \text{ ppm})^2 (8 \text{ hours}) = k = 1,874,048 \text{ ppm-hr}$

Total uncertainty/modifying factor: 60

Uncertainty factor: 30

Intraspecies: 3 - response to irritant gas is not likely to vary greatly among humans

Interspecies: 10 - extent of edema in the animal lungs was not specified

Modifying factor: 2 - very limited overall database

AEGL-2 Values for Ethylenediamine [mg/m ³]			
30 minutes	1 hour	4 hours	8 hours
32 ppm [79]	23 ppm [56]	11 ppm [28]	8.1 ppm [20]

NOTE THAT hypersusceptible individuals, i.e. sensitized to EDA, may experience effects beyond the scope of AEGL-2.

Data Relevant to AEGL-3

- ▶ *No quantitative human exposure data.*
- ▶ Rat lethality threshold from Smyth et al. (1951) range-finding study: 0/6 deaths from 8 hours at ~1000 ppm (2000 ppm nominal); 6/6 deaths at 4000 ppm EDA (nominal). Effects on the animals (besides death) were not described.
- ▶ Lethality threshold unclear in multiple-exposure study of Pozzani and Carpenter (1954): rats exposed 7 hrs/day for ≤ 30 days to 225 or 484 ppm had liver, kidney, and lung lesions; first deaths on 3rd and 4th exposure days, respectively.

AEGL-3

Key study: Smyth et al., 1951

Toxicity endpoint: Estimated lethality threshold for rat 8-hour exposure to ~1000 ppm EDA (2000 ppm nominal).

Scaling: $C^2 \times t = k$ ($n = 2$; ten Berge et al., 1986)
 $(1000 \text{ ppm})^2 (8 \text{ hrs}) = k = 8,000,000 \text{ ppm-hrs}$

Total uncertainty/modifying factor: 60

Uncertainty factor: 30

Intraspecies: 3 - response to irritant gas is not likely to vary greatly among humans

Interspecies: 10 - values were based on only one species, one experiment

Modifying factor: 2 - very limited overall database

AEGL-3 Values for Ethylenediamine [mg/m ³]			
30 minutes	1 hour	4 hours	8 hours
67 ppm [164]	47 ppm [116]	24 ppm [58]	17 ppm [41]

NOTE THAT hypersusceptible individuals, i.e. sensitized to EDA, may experience effects beyond the scope of AEGL-3.

SUMMARY OF AEGL VALUES FOR ETHYLENEDIAMINE

Level	30 minute	1 hour	4 hours	8 hours	Endpoint (Reference)
AEGL 1	11 ppm [27 mg/m ³]	7.8 ppm [19 mg/m ³]	3.9 ppm [9.6 mg/m ³]	2.8 ppm [6.8 mg/m ³]	NOAEL for rats exposed to 59 ppm (7 hrs/day, 30 days) (Pozzani and Carpenter, '54)
AEGL 2	32 ppm [79 mg/m ³]	23 ppm [56 mg/m ³]	11 ppm [28 mg/m ³]	8.1 ppm [20 mg/m ³]	Bronchiolar edema, cloudy swelling of rat and guinea pig kidneys: 1000 ppm for 8 hrs (Carpenter et al., 1948)
AEGL 3	67 ppm [164 mg/m ³]	47 ppm [116 mg/m ³]	24 ppm [58 mg/m ³]	17 ppm [41 mg/m ³]	Rat lethality threshold: 2000 ppm for 8 hrs (Smyth et al., 1951)

Summary of Response of Rats Exposed for Thirty Days to Ethylenediamine

Nominal concentration, ppm.....	1,000	0	500	0	250	0	125	0
Observed concentration, ppm.....	484	..	225	..	132	..	59	..
Mean wt. of rats at start, gm.....	143.5	141.4	134.8	131.9	149.2	147.9	157.0	159.4
Mean wt. gain of surviving rats, gm.	..	+81.1	+18.0<	+97.2	+85.2	+84.3	+75.7	+82.8
Liver wt. as % of body wt.....	4.14>	3.80	4.04	4.16	3.52	3.55
Kidney wt. as % of body wt.....	1.00>	0.77	0.81	0.79	0.79	0.78
Uninfected rats	30	30	20	28	26	27	30	29
Toxic deaths	30	0	16	0	0	0	0	0
Mean no. of days to death.....	11.4	..	17.2
Sets of tissues examined from <u>uninfected</u> rats	27	30	17	25	26	27	29	29
Sets with major pathology.....	8	0	5	0	1	0	0	0
Sets with minor pathology.....	27	0	14	6	5	3	1	13

< = Deviation below control is statistically significant.

> = Deviation above control is statistically significant.

484 ppm: days 3, 5, 7 } 1st deaths
225 ppm: days 4, 5, 9 }

**PHOSPHORUS TRICHLORIDE
DRAFT AEGL DEVELOPMENT**

**NAC/AEGL -13
New Orleans, LA
March 11-12, 1999**

PCl₃ AEGL Development

- **Colorless, fuming liquid**
- **Decomposes rapidly to phosphonic acid, hydrogen chloride, and pyrophosphonic acids**
- **Contact irritant, tissue destruction due to decomposition products**
- **Systemic toxicant ?? renal toxicity**

PCl₃ Data Summary

- **Lethal Toxicity**

ACUTE LETHALITY OF PHOSPHORUS TRICHLORIDE IN LABORATORY SPECIES		
Species	Lethality Value	Reference
Rat	4-hr LC₅₀ : 104.3 ppm	Weeks et al., 1964
Cat	lethality at 306 min, 694 ppm	Butjagin,1904
Cat	lethality at 3 hours, 623 ppm	Butjagin,1904
Guinea pig	4-hr LC₅₀ : 50.1 ppm	Weeks et al.,1964
Guinea pig	lethality at 3 hours, 623 ppm	Butjagin,1904

- **Definitive quantitative data limited to that by Weeks et al.,1964**
- **Exposure-response data unavailable**

PCl₃ Data Summary

- **Nonlethal Toxicity**

- **1 ppm for 1 hr - no effect in human (Tharr and Singal, 1980)**

- **Butjagin (1904) guinea pigs and cats (only 1 to 3 per experiment)**

0.71 ppm for 6 hrs	-	restlessness, salivary and nasal secretions, irregular respiration, coughing
or		
1.78 - 5.36 ppm for 6 hrs		
50 - 90 ppm for 1 hr	-	severe signs of toxicity (cats and guinea pigs)
135 - 303 ppm for 6 hrs	-	signs of severe irritation, labored respiration, pulmonary edema, severe tissue damage

PCl₃ AEGL-1

AEGL-1 VALUES FOR PHOSPHORUS TRICHLORIDE				
AEGL Level	30-min	1-hr	4-hr	8-hr
AEGL-1	0.08 ppm	0.06 ppm	0.03 ppm	0.02 ppm

PCl₃ AEGL-2

- **5.36 ppm for 6 hrs (Butjagin, 1904) - restlessness, ocular and nasopharyngeal irritation**
- **A conservative estimate of an exposure for AEGL-2 effects**
- **Time scaling as for AEGL-1: $n = 2$**
- **Uncertainty factor application as for AEGL-1: $10 \times 3 = 30$**

AEGL-2 VALUES FOR PHOSPHORUS TRICHLORIDE				
AEGL Level	30-min	1-hr	4-hr	8-hr
AEGL-2	0.25 ppm	0.18 ppm	0.09 ppm	0.06 ppm

PCl₃ AEGL-3

- **4-hr LC₅₀:** 104.3 ppm (rat)
(Weeks et al. , 1964) 50.1 ppm (guinea pig)
- **Basis of AEGL-3 :** 3-fold reduction of 50.1 ppm (16.7 ppm)
Represents a nonlethal exposure based upon
comparison to Butjagin (1904) data
- **Time scaling:** as for AEGL-1 and AEGL-2
- **Uncertainty factor application as for AEGL-2 and 3:** 10 x 3 = 30

AEGL-3 VALUES FOR PHOSPHORUS TRICHLORIDE				
AEGL Level	30-min	1-hr	4-hr	8-hr
AEGL-3	1.6 ppm	1.1 ppm	0.56 ppm	0.39 ppm

PCl₃ DRAFT AEGL VALUES

DRAFT AEGL VALUES FOR PHOSPHORUS TRICHLORIDE (ppm)					
Classification	30-min	1-hour	4-hour	8-hour	Endpoint (Reference)
AEGL-1	0.08	0.06	0.03	0.02	Mild respiratory irritation in cats and guinea pigs exposed to 0.71 ppm for 6 hrs or 1.78 ppm for 1 hr (Butjagin, 1904)
AEGL-2	0.25	0.18	0.09	0.06	Notable respiratory distress and irritation in cats and guinea pigs exposed to 5.36 ppm for 1 hr. (Butjagin, 1904)
AEGL-3	1.6	1.1	0.56	0.39	Estimated lethality threshold based upon 3-fold reduction of guinea pig 4-hr LC₅₀ (50.1 ppm/3 = 16.7 ppm) (Weeks et al., 1964)

- **Application of Modifying Factor of 2 for deficient data set ?**

PCl₃ AEGL ISSUES

- **Data set**
 - very limited
 - exposure-response relationship uncertainties

- **Degradation of PCl₃ in moist air**
 - 4 and 8-hour AEGLs appropriate ?

- **Butjagin (1904) report**
 - not GLP
 - no. and condition of animals
 - uncertainties regarding techniques
 - analytical
 - generation of test atmosphere

- **Weeks et al. (1964)**
 - generation of test atmosphere
 - analytical

**PHOSPHORUS OXYCHLORIDE
DRAFT AEGL DEVELOPMENT**

**NAC/AEGL -13
New Orleans, LA
March 11-12, 1999**

POCl₃ AEGL Development

- **Colorless, fuming liquid**
- **Decomposes rapidly to phosphoric acid, hydrogen chloride**
- **Contact irritant, tissue destruction due to decomposition products**
- **Systemic toxicant ??**

POCl₃ Data Summary

- **Lethal Toxicity**

ACUTE LETHALITY OF PHOSPHORUS OXYCHLORIDE IN LABORATORY SPECIES		
Species	Lethality Value	Reference
Rat	4-hr LC₅₀: 48.4 ppm	Weeks et al., 1964
Rat	4-hr LC₅₀: 32 ppm (not verified)	RTECS, 1998
Rat	1-min 100% lethality: 25,462 ppm	Monsanto, 1991
Guinea pig	4-hr LC₅₀: 52.5 ppm	Weeks et al., 1964

- **Definitive quantitative data limited to that of Weeks et al., 1964**
- **Exposure-response data unavailable**

POCl₃ Data Summary

- **Nonlethal Toxicity**

- Humans**

- **irritation, respiratory distress (qualitative data only) (Rosenthal et al., 1978)**
 - **1.6 to 11.2 ppm (no duration data); ocular and respiratory tract irritation, latent responses (Sassi et al., 1954)**

- Animals**

- **acute exposures produce irritation, no quantitative exposure data**

POCl₃ AEGL-1

- **Insufficient data**
- **AEGL-1 values not determined**

POCl₃ AEGL-2

- **Insufficient data**
- **AEGL-2 values not determined**

POCl₃ AEGL-3

- **4-hr LC₅₀ in rat:** 48.4 ppm (Weeks et al. , 1964)
- **Basis of AEGL-3 :** estimate of lethality threshold (16.1 ppm) by 3-fold reduction of rat 4-hr LC₅₀ ppm
- **Time scaling:** n=2 for 30 min. and 1-hr; n=1 for 4 and 8 hrs; insufficient data for empirical derivation of n
- **Uncertainty factor application**
 - **Interspecies UF = 10;** uncertainty regarding sensitivity of humans relative to animal models.
 - **Intraspecies UF = 3;** the mechanism of contact irritation and subsequent tissue damage (due, in part, to hydrogen chloride and phosphonic acid degradation products) is not likely to vary by an order of magnitude among individuals

POCl₃ AEGL-3

AEGL-3 VALUES FOR PHOSPHORUS OXYCHLORIDE				
AEGL Level	30-min	1-hr	4-hr	8-hr
AEGL-3	1.52 ppm	1.07 ppm	0.54 ppm	0.27 ppm

POCl₃ DRAFT AEGL VALUES

DRAFT AEGL VALUES FOR PHOSPHORUS OXYCHLORIDE (ppm)					
Classification	30-min	1-hour	4-hour	8-hour	Endpoint (Reference)
AEGL-1	ND	ND	ND	ND	not determined; insufficient data
AEGL-2	ND	ND	ND	ND	not determined; insufficient data
AEGL-3	1.52	1.07	0.54	0.27	Estimated lethality threshold based upon 3-fold reduction of rat 4-hr LC₅₀ (48.4 ppm/3 = 16.1 ppm) (Weeks et al., 1964)

POCl₃ AEGL ISSUES

- **Data set**
 - very limited (no data consistent with AEGL-1 and AEGL-2)
 - lethality data limited to two species
 - exposure-response relationship uncertainties

- **Degradation of POCl₃ in moist air**
 - 4 and 8-hour AEGLs appropriate ?

- **Weeks et al. (1964)**
 - generation of test atmosphere
 - analytical techniques

PCl₃ INCIDENT 1

- ESTIMATED 6,000-12,000 LBS RELEASED FROM OVERFILLING RR TANK CAR ON 4-17-88
- POOL APPROXIMATELY 1,400 FT², GENERATED PLUME WHICH WAS MISTED TO LIMIT SPREAD
- WINDS "LIGHT SW", TEMPERATURE 60°
- 22 SQUARE BLOCKS EVACUATED, (MAX-DISTANCE APPROX. 3/4 MI), 417 CITIZENS WENT TO EMERGENCY ROOMS, 2 HOSPITALIZED OVERNIGHT
- EYE & RESPIRATORY IRRITATION MAIN COMPLAINTS
- ARCHIE RESULTS, USING STABILITY CLASS C
 - VAPOR EVOLUTION RATE=94LB/MIN, DURATION=127.8 MIN
 - LIMIT CONC=0.25PPM(½ HR.AEGL-2) GIVES DOWNWIND HAZARD DISTANCE=12174 FT(2.3MI)
 - LIMIT CONC=1.0PPM GIVES DOWNWIND HAZARD DISTANCE=5685 FT
 - PREDICTED MAX. GROUND CONC.=1883PPM AT 100 FT



BROOKLYN

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62201

62207

62205

SAINTE

SAUGET

DOWNTOWN-PARKS AIRPORT

CAHOKIA

PARKS COLLEGE AIRPORT

CENTREVILLE

66

Martin Luther King Mem. Bridge (Toll)

Jefferson (Toll)

Expansion Gateway Arch

Nat. Mem.

McArthur Bridge

Missouri Illinois

Southern

Airon

Hob Hollow

David School

Kirkier

Edwards

Waller

Waller

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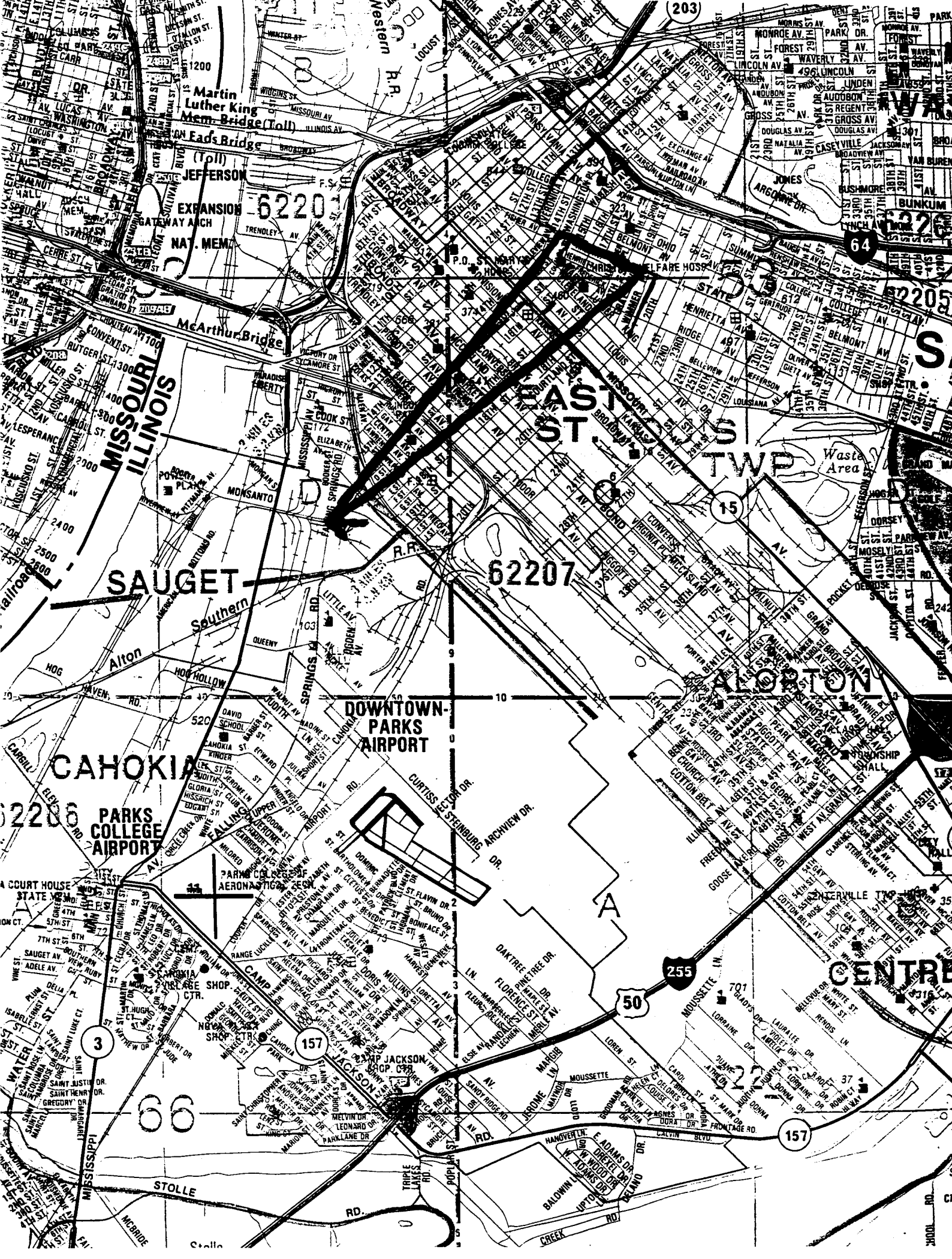
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PCl₃ INCIDENT 2

- ESTIMATED MAX. 55 LBS RELEASED FROM FAILURE OF RUPTURE DISK ON 7-31-88
- RESULTING PLUME WAS VISUALLY TRACKED AND BOUNDED BY PLANT PERSONNEL, DISSIPATED APPROX. 2 MI DOWNWIND
- WINDS S-SW 5-7 MPH, TEMPERATURE 82°
- 244 CITIZENS WENT TO EMERGENCY ROOMS, 7 HOSPITALIZED OVERNIGHT AND 1 HOSPITALIZED 3 DAYS (PRE-EXISTING ASTHMA)
- EYE, NOSE, AND THROAT IRRITATION MAIN COMPLAINTS
- ARCHIE RESULTS, USING STABILITY CLASS C
 - VAPOR RELEASE RATE=11 LB/MIN, DURATION=5 MIN, RELEASE TEMP=100°
 - LIMIT CONC=0.25PPM(½ HR.AEGL-2) GIVES DOWNWIND HAZARD DISTANCE=3826 FT(0.73MI)
 - LIMIT CONC=1.0PPM GIVES DOWNWIND HAZARD DISTANCE=1807 FT
 - PREDICTED MAX. GROUND CONC.=45.9PPM AT 139 FT



Martin Luther King Mem. Bridge (Toll)

Eads Bridge

JEFFERSON

EXPANSION 62201

NAT. MEM.

McArthur Bridge

MISSOURI ILLINOIS

SAUGET

62207

DOWNTOWN PARKS AIRPORT

CAHOKIA

PARKS COLLEGE AIRPORT

MORTON

CENTRE

50

255

157

66

3

STOLLE

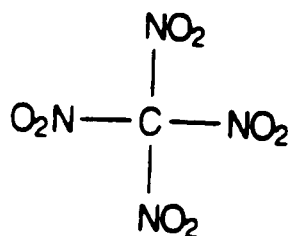
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**ACUTE EXPOSURE GUIDELINE LEVELS (AEGLs)
FOR
TETRANITROMETHANE (TNM)**



March 11-12, 1999

ORNL Staff Scientist: Sylvia Milanez
Chemical Manager: Kyle Blackman
Chemical Reviewers: George Rodgers, Richard Thomas

INTRODUCTION

- ▶ TNM is explosive liquid used as oxidizer in rocket propellants, to increase octane of diesel fuels. Its formation as an impurity (fumes) during TNT (trinitrotoluene) production historically accounts for interest in TNM toxicity.
- ▶ One current U.S. producer: Hummel Chemical Co; amount produced not available. U.S. production in 1977 was >1000 pounds (HSDB, 1999).
- ▶ No quantitative human exposure data. **Impure** TNM (from TNT production) caused irritation of the eyes, nose, throat, dizziness, chest pain, dyspnea, pulmonary edema, pneumonia, methemoglobinemia, cyanosis, and death.
- ▶ Effects in animals: respiratory and eye irritation, lung vascular congestion, pulmonary edema, bronchopneumonia, and lung tumors in rats and mice.
- ▶ TNM had a pungent, acrid odor; no human odor threshold data were found.

Data Relevant for AEGL-1

- ▶ No quantitative human data - anecdotal reports of inhalation of TNM-containing fumes emitted during TNT production (Koelsch, 1917; Sievers et al., 1947; Hager, 1949).
- ▶ Cats exposed for 6 hours to ~ 0.1-0.4 ppm TNM fumes emitted from TNT production wastewater had slight lacrimation (Sievers et al., 1947).
- ▶ **No toxic effects in F344/N rats and B6C3F1 mice from exposure to 2 ppm TNM 6 hrs/day for 2 weeks (5 d/wk) (NTP, 1990). At the next higher conc. (5 ppm), mice had inflammation of nasal mucosa.**
- ▶ Dogs exposed to 6.35 ppm TNM for 6 months (6 hrs/day, 5 d/wk) coughed, were lethargic, appeared “unthrifty”, did not eat first 2 days (Horn, 1954).

AEGL-1

Key study: NTP, 1990

Toxicity endpoint: No effect on mice or rats from exposure 6 hrs/day for 2 weeks (5 d/wk). Use single 6-hour exposure for derivation.

Scaling: $C^2 \times t = k$ ($n = 2$; tenBerge et al., 1986).
 $(2 \text{ ppm})^2 (6 \text{ hrs}) = k = 24 \text{ ppm-hrs}$

Total uncertainty factor: 10

Intraspecies: 3 - response to irritant gas is not likely to vary greatly among humans

Interspecies: 3 - toxicity of TNM did not vary greatly between two species; key study was repeat-exposure

AEGL-1			
30 minutes	1 hour	4 hours	8 hours
0.69 ppm (5.6 mg/m ³)	0.49 ppm (3.9 mg/m ³)	0.24 ppm (2.0 mg/m ³)	0.17 ppm (1.4 mg/m ³)

Data Relevant for AEGL-2

- ▶ **B6C3F1 mice (5/sex) exposed to 5 ppm TNM for 6 hrs/day for 2 weeks (5 d/wk) had reddened lungs and lowered body weights (NTP, 1990).**
- ▶ **Rats (100 males) exposed 2 weeks continuously to 3.5 ppm TNM were lethargic, had dyspnea, lower body weights, pneumonitis, bronchitis, tracheitis, and edema (Kinkead et al., 1977).**

AEGL-2

Key study: NTP, 1990

Toxicity endpoint: Inflamed lungs and weight loss in B6C3F1 mice exposed to 5 ppm TNM 6 hrs/day for 2 weeks (5 d/wk). Use single 6-hour exposure for derivation.

Scaling: $C^2 \times t = k$ (n = 2; tenBerge et al., 1986)
(5 ppm)² (6 hrs) = k = 150 ppm-hrs

Total uncertainty factor: 10

Intraspecies: 3 - response to irritant gas not is likely to vary greatly among humans

Interspecies: 3 - most sensitive species and multiple-exposure study were used

AEGL-2			
30 minutes	1 hour	4 hours	8 hours
1.7 ppm (14 mg/m ³)	1.2 ppm (9.8 mg/m ³)	0.61 ppm (4.9 mg/m ³)	0.43 ppm (3.5 mg/m ³)

Data Relevant for AEGL-3

- ▶ 4-hour exposure yields LC₁ of 9.4 ppm for rats and 20.5 for mice (LC₅₀ of 17.5 ppm; 54.4 ppm); 10 males/conc./strain tested (Kinkead et al. 1977). See lethargy, nose and eye irritation, lung congestion and hemorrhage.
- ▶ **Rats and mice (5/sex) exposed 6 hrs/day for 2 wks (5 d/wk) to 10 ppm had low weight gain; mice had reddened lungs (one treatment-unrelated death on day 8;) (NTP, 1990). High mortality at next conc. (25 ppm); 10 ppm is lethality threshold for both species.**

Advantage of NTP (1990) vs. Kinkead et al. (1977)

- (1) 10 ppm is more conservative estimate of lethality threshold, and is based on male and female rats and mice for 10 exposures vs. one exposure in only male rats in Kinkead study (mouse LC₁ = 20.5 ppm)
- (2) Method NTP (1990) used to measure TNM concs. (Miran Infrared gas analyzer) perhaps more sensitive than colorimetric method used by Kinkead
- (3) Values more consistent with AEGL-1 and AEGL-2 since same rat strain (F344/N) and both sexes tested; Kinkead used Sprague-Dawley males

AEGL-3

Key study: NTP, 1990

Toxicity endpoint: Threshold of lethality for rats and mice. Lung inflammation in mice, weight loss in both species at 10 ppm, 6 hrs/day for 2 wks (5 d/wk). High mortality (1-4 exposures) and lung lesions in both species at next conc. tested (25 ppm).

Scaling: $C^2 \times t = k$ (N = 2; ten Berge et al., 1986)
(10 ppm)² (6 hrs) = k = 600 ppm-hrs

Total uncertainty factor: 10

Intraspecies: 3 - response to an irritant gas is not likely to vary greatly among humans

Interspecies: 3 - similar toxicity in two species; multiple-exposure study

AEGL-3			
30 minutes	1 hour	4 hours	8 hours
3.5 ppm (28 mg/m ³)	2.4 ppm (20 mg/m ³)	1.2 ppm (9.8 mg/m ³)	0.87 ppm (6.9 mg/m ³)

SUMMARY OF AEGL VALUES FOR TETRANITROMETHANE (ppm [mg/m³])					
Level	30'	1 hr	4 hrs	8 hrs	Endpoint (Reference)
AEGL-1	0.69 [5.6]	0.49 [3.9]	0.24 [2.0]	0.17 [1.4]	Rat, mouse NOAEL (2 ppm, 6 hrs/day, 2 wks; NTP 1990).
AEGL-2	1.7 [14]	1.2 [9.8]	0.61 [4.9]	0.43 [3.5]	Mouse lung inflammation (5 ppm; NTP, 1990).
AEGL-3	3.5 [28]	2.4 [20]	1.2 [9.8]	0.87 [6.9]	Rat, mouse lethality thres-hold (10 ppm; NTP 1990).

PROPOSED AEGL VALUES (ppm)						
Level	30'	1 hr	4 hrs	8 hrs	Endpoint	
AEGL-1	0.69	0.49	0.24	0.17	NOAEL in rats, mice	n = 2 UF = 10 (NTP, 1990)
AEGL-2	1.7	1.2	0.61	0.43	Reddened lungs in mice	
AEGL-3	3.5	2.4	1.2	0.87	Lethality threshold in rats and mice	
Alternate AEGL-3 values (ppm)						
AEGL-3	2.7	1.9	0.94	0.66	Rat LC ₁ (Kinkead et al., 1977)	
AEGL-3	4.9	2.4	0.61	0.31	10 ⁻⁴ lifetime cancer risk ¹ (NTP, 1990) n = 1; UF = 1	

¹Unit risk calculated using the linearized multistage model from the female mouse 103-week lung carcinogenicity data (NTP, 1990). COT methodology used to extrapolate to single exposure.

A. INTRODUCTION - THE EARLY YEARS

The development of aviation fuels directly parallels the history of manned, powered flight. The key contribution of the Wright Brothers that enabled their first flights of significant duration was an ingenious combination of movable surfaces that provided controllability. Another key that the Wright Brothers were wise enough to recognize was the internal combustion engine. The lack of a lightweight power plant was a principal handicap to the success of powered flight at the end of the 19th century. All attempts to adapt the most readily available machine, the steam engine, ended in failure. Etienne Lenoir, a Frenchman, devised the first internal combustion engine in 1860. He burned coal oil gas in air to provide a working fluid to replace the steam ordinarily used in reciprocating engines. The four stroke internal combustion engine was born in 1876 when N. A. Otto and Eugen Langen fed coal oil gas to a machine that proved to be much more efficient than the steam engines of that day. Another German, Karl Benz, put the first reliable Otto engine on the road in 1885, and launched the automobile age.

Despite the success demonstrated by Benz, America's Samuel Langley turned to the steam engine for his first aircraft. Langley's unmanned aircraft flew successfully in 1896 and opened the door to the great potential of powered flight. Langley's steam engine, however, could not provide sufficient power for manned flight. With funding provided by Congress to promote manned flight, Langley's assistant, Charles Manley, in 1901 constructed a 52 HP internal combustion engine based on a design by Stephen Balzer. Manley's engine weighed 2.4 lbs/HP, about one-tenth as much as a light weight steam engine. It was a truly remarkable engine for its time, and can be considered as the first real aircraft engine.

The petroleum industry was established in the mid-19th Century to provide coal oil and kerosene for illumination. By the time Otto and Benz were building their internal combustion engines, these materials were readily available for use as fuels. It was soon determined that successful atomization in the carburetor required a more volatile distillate. By the time the first aircraft engines were being built, gasoline was a well established commodity for the thousands of automobiles on the road.

The Wright Brothers built their own internal combustion engine for their manned flights. The four cylinder water cooled engine weighed 180 lbs and developed 12 HP. This engine, fueled by several cans of Standard Oil motor gasoline, ushered the world, on December 17, 1903, into a new era. The Wright Brothers airplane fulfilled the passion for flight that had reached a fever pitch during the late 19th Century. Despite its central role, gasoline was taken for granted. This was mainly because the light fraction distilled from crude during the manufacture of kerosene contained natural properties that exceeded the demands of the engines of that era. The first decade of flight brought to the fore the importance of fuel volatility and gravity, but it was World War I that focused attention on the need for real fuel development, which would lead to a gasoline that could be burned in an internal combustion engine without detonating. From that time forward the advancement of aircraft engines has placed increasing demands on the fuel. Fuel developers have responded and contributed significantly to the expansion of aviation capabilities during the 20th Century.

The purpose of this paper is to outline the development of aviation fuels in the United States during the 20th Century. This introduction is followed by separate sections on Aviation Gasoline and Turbine Engine Fuels. Those sections are followed by one discussing the development and importance of fuel additives. Another section on Missile Fuels is followed by one discussing the future for aviation fuels.

This paper relies very heavily on a few significant references. These include AIAA Paper No. 69-779 entitled "Milestones in Aviation Fuels". It was written by W. G. Dukek and D. R. Winans of the Esso Research and Engineering Company and A. R. Ogston of Esso International. It was presented at the AIAA Aircraft Design and Operations Meeting in 1969. Another prominent reference is AFWAL-TR-87-2062 entitled "Military Jet Fuels, 1944-1987". It was written by Charles R. Martel of the Fuels Branch at Wright-Patterson Air Force Base. Three additional important references were written by James R. McCoy, also of the Fuels Branch at Wright-Patterson. These include "A Short History of the Development of MIL-T-25524 Thermally Stable Fuels", written in 1974; "Special Military Fuels: JP-TS, JP-7, JP-9, and JP-10", written in 1980 and presented at the Military-Industry Energy Symposium at San Antonio, TX; and "The Development of Turbine and Ramjet Missile Fuels, 1973-1991", written in 1991. Additional information was obtained from AIAA Paper No. 96-0403, entitled, "JP-8+100: Development of High Thermal Stability Jet Fuel", by S. P. Heneghan, S. Zabarnick, and D. R. Ballal of the University of Dayton, and W. E. Harrison III of the Air Force Wright Laboratories; a paper entitled "Fundamentals of Jet Fuel Lubricity" by Patricia D. Liberio and Jeffrey A. Pearce of the Air Force Wright Laboratories; and a Navy report entitled "High-Energy Airbreathing Missile Fuels", by William Burdette. The reader is directed to these documents, and the references cited therein, for additional details that are beyond the scope of this paper.

B. AVIATION GASOLINE

The first World War (1914-18) provided considerable impetus to aircraft and engine development. Fuel characteristics soon became limiting factors that lead to the first real fuel development efforts. Prior to the war, engines were generally operated with the lightest and most volatile fuels that were available at the time. The first observation of engine knock (called "pinking" at the time) was attributed to heavy fuels that caused engines to run hot. To insure satisfactory operation, the aviation pioneers insisted on "high test" gasoline, which connotated, at that time, fuels of light specific gravity. The first United States Government specification for the purchase of gasoline appeared in 1907 as U. S. Navy Specification Number 24G.5. Its modest requirements called for: "High grade refined gasoline free from all impurities, having a gravity of 70oBe, and requiring that no residue be left in a platinum dish after one hour in boiling water".

World War I presented the need for increased speed and higher altitude ceilings for aircraft. To get more power from an engine an increase in the compression ratio, which increased the capacity for air and fuel, was required. As early as 1915 it was recognized that air density decreased with altitude, and experiments with superchargers were initiated in Great Britain. The aviation used by the British and French during the early years of the war came from aromatic crudes of the Dutch East Indies and British Borneo. Because this fuel had an aromatic content as high as 30%, it displayed high anti-detonation value in engines, and did not immediately limit the development of more powerful engines.

Germany's pre-war crude supplies had come from Mexico and Rumania. As the British blockade effectively shut off tanker shipments from overseas, Romania became the principal source of supply. Oil supplies for the German forces in Western Europe were limited and forced Germany to resort to substitute fuels with inferior properties. Blends of kerosene, benzol, and potato alcohol were often used in heavy bombers, while remaining petroleum fuels were reserved for fighter aircraft.

As the war proceeded German submarine attacks began to reduce the availability of fuel from the Far East for the Allies. In 1917 America was requested to supply the major portion of the oil products so badly needed. At that time there were three grades of gasoline being marketed in the U. S. One of these, Grade X, with a distillation end point between 320°F and 374°F was the type usually exported. When the flood of Grade X fuel began to reach the fighting front, it was found to be nearly unacceptable for combat use! Serious engine overheating was experienced when the fuel supply was switched from the highly aromatic East Indian crude to the U. S. Grade X. It was not understood at the time, but the East Indian derived fuels had, by modern standards, octane number ratings of 65-70, while the U. S. fuels, refined principally from Pennsylvania and Oklahoma crudes, had octane numbers of only 45-55. The only remedy for the poor fuel was to blend in as much as 20% of benzol. In August 1917, Ernst W. Dean and Clarence Netzer at the U. S. Bureau of Mines began to investigate suitable fuels for aircraft engines. In addition to Grade X, two other grades of gasoline were being marketed, Motor gasoline (distillation end point 375°F and above), and Grade H (end point below 320°F). Dean and Netzer concluded that high volatility and a relatively low distillation end point were all that were required for suitable aviation fuels. As a result, three grades of fuel were supplied to the military thereafter. "Domestic Aviation" had the lowest volatility and was used primarily for low-powered engines in training aircraft. "Export Grade X" still enjoyed the highest availability, and "Fighting Grade", with the highest volatility was available in limited quantities.

To improve fighting grade fuel, the Bureau of Mines, in May 1918 asked the Atlantic Refining Company to furnish for comparative testing, 11 grades of gasoline covering a range from ordinary motor fuel of relatively low volatility to a special close-cut grade of high volatility. Each of the fuels was run in a combat type aircraft engine at the Langley Field laboratories of the Bureau of Standards. The results of the engine tests proved disappointing in that the differences found among the fuels, as to developed power, economy, high altitude performance, etc. were only + or - 5%. The problem with these tests was the fact that they were run at a single, rather modest, engine compression ratio. Real differences, especially in anti-knock qualities, would have become apparent if higher compression ratios had been examined. A second series of tests were conducted with the same engine in order to compare fuels from East Indian crudes against Export Aviation Gasoline. Again, the test showed no significant difference in power development, even though the East Indies fuels were recognized to be superior in service. It was correctly concluded, and subsequent experience was to show conclusively, that the volatility has very little to do with the power potential of a fuel.

Knocking, or detonation, was observed in motor vehicle engines early in their use, and by 1906 it was being actively investigated by Professor Bertram Hopkinson and his young assistant Harry Ricardo at Cambridge University. In early aircraft engines, knocking was thought to be a result of inadequate engine cooling. The understanding of the knock mechanism and the crucial role played by the fuel itself was to have a profound effect on both the aviation and petroleum industries. World War I accentuated the knock problem because every program to develop more powerful engines was ultimately limited by the detonation characteristics of the fuel. Hopkinson observed in 1906 that pre-ignition and detonation were two distinct phenomena, and that the latter was responsible for the former. Pre-ignition (the tendency of fuel to ignite ahead of the spark due to the presence of localized hot spots) was later proved to be the real wrecker of lightly built aircraft engines. It had been substantially ignored because it caused no alarming noises, as did detonation.

Harry Ricardo's first independent work after leaving Cambridge was conducted from 1916 to 1918 on the investigation of the detonation qualities of fuels using a single cylinder supercharged engine of his own design. He compared the relative merits of aromatic, naphthenic, and paraffinic fuels by varying the boost pressure until detonation occurred. He was able to show that aromatics were the best while the straight-chain paraffins were the worst in detonation qualities. He was also able to prove Hopkinson's theory that detonation was responsible for pre-ignition. This work led the Asiatic Petroleum Company in 1919 to hire Ricardo to set up a research laboratory to investigate further the phenomena of detonation and its relation to fuel quality. Ricardo designed a variable compression test engine and had associates Henry Tizard and David Pye investigate the chemical and thermodynamic properties of the fuels that would be run in the engine. Tizard and Pye established three important principles: (1) Chemical compositions of fuels had a profound effect upon engine performance; (2) At a single compression ratio, differences in power development were minor; (3) The more detonation resistant the fuel, the higher the compression ratio that could be used, and, therefore, the more efficient and powerful the engine could be. The findings of Ricardo and his group appeared in 1923 in a classic report entitled: "The Internal Combustion Engine". In the report Ricardo pointed out that the

phenomenon of detonation is by far the most important factor in determining the quality of a fuel, and that it depends primarily on its chemical composition.

Ricardo realized that in order to devise a reproducible method for rating fuels, good reference fuels would be needed. He had found that pure toluene showed the highest anti-knock quality when used as a fuel. He decided to express the detonation quality of fuels in terms of their relative toluene content. Asiatic Petroleum prepared a quantity of aromatic free reference fuel by acid treating it. Blends of this fuel with pure toluene were run in the test engine to determine the detonation point versus the percentage of toluene in each blend. Using this Toluene Rating System, the highest useful compression ratio could be established for any test engine with a given fuel.

During the pre-war period when detonation was being investigated by Hopkinson, Ricardo, and Gibson in Britain, knock in engines became a serious problem to the Dayton Engineering Laboratories (Delco) of Charles Kettering in the U. S. Kettering was concerned because his system of battery ignition in automobile engines was blamed for knock. In addition, Delco was faced with a rash of failures in the kerosene powered engines they sold with their lighting generator sets. The supposedly superior Pennsylvania kerosenes caused detonation, while the poor quality illuminating grade California kerosenes performed well. Kettering asked his assistant, Thomas Midgely, to investigate the detonation characteristics of fuels. Kettering and Midgely used a standard air-cooled Delco-Lite engine with modified cylinder heads for different compression ratios in their first experiments. They developed a "bouncing pin" device to measure differences in detonation pressures. They determined that detonation was related to both the compression ratio and the different molecular structure of the fuel. Theorizing that knock resulted because some of the vaporized kerosene was liquefying on the cylinder walls, Kettering and Midgely thought that a dark colored kerosene would absorb more heat energy, and thus be less likely to condense on the cylinder walls. They thought that they had confirmed this theory when they added iodine to kerosene to make it dark, and found that knock was reduced. This was the beginning of what was to become a very long line of anti-knock additives to be investigated. A vigorous program of research was launched in 1920 to find compounds that could be added to gasoline to suppress knock. Some 30,000 compounds had been screened, when, on December 9, 1921, Midgely and his assistant, Thomas Boyd, discovered the remarkable anti-knock properties of tetraethyl lead, a discovery that ranks as the single most important achievement in the development of gasoline fuels. Although nearly ten years were to lapse before this remarkable compound became widely accepted as an essential component of aviation gasoline, its use opened the way to the great advances in anti-knock value of fuel that made possible the high power output and efficient aircraft engines that dominated military and commercial aviation until the arrival of the gas turbine.

In 1921 the Cooperative Fuel Research (CFR) Committee was formed, including members of the Society of Automotive Engineers (SAE), the National Automobile Chamber of Commerce, and the American Petroleum Institute (API), to: study problems involved in the mutual adaptation of the fuel and engine to each other to the end of the national economy and internal combustion engine efficiency". Between 1921, when the CFR was organized, and 1926, nearly all of the major oil companies and several universities had set up knock testing laboratories. During 1926, the CFR requested that the Bureau of Standards make a survey of the methods for measuring the anti-knock qualities of fuels. It was found that there was very little common ground, and almost no correlation among various laboratories. Many different engines were in use, and although repeatability was possible on the same engine in one laboratory, results were almost impossible to duplicate by others, due to differences in operating conditions. This problem was compounded by the lack of suitable reference fuels. A significant milestone in aviation fuels research was reached during 1927, when Graham Edgar of the Ethyl Gasoline Corp, proposed the adoption of two pure paraffin hydrocarbons as reference fuels for knock rating. The first of these, normal heptane (C₇H₁₆), was selected because it would knock almost any conditions in an engine. The second compound, the isomer of normal octane known as iso-octane, was found by Edgar to have a knock resistance higher than any gasoline. Additionally, the two fuels were almost identical in volatility, chemical composition, and other physical properties. Edgar demonstrated that the two fuels could be blended together to duplicate the knocking characteristics of any known motor fuels. Thus began the Octane Number scale, which is still the standard method for quoting the anti-knock quality of gasoline. By 1932, industry had generally adopted a standardized method for knock rating, using an engine designed by H. L. Horning of the Waukesha Motor Company for the CFR Committee, and Edgar's fuel standards.

Until about 1912, petroleum refining was more art than science. Production depended mostly on the stillman's skill with a thermometer and gravity stick for the separation of refinery streams. As motor fuel became in short supply due to the rapid increase in automobiling after the turn of the century, refiners were looking into better methods for increasing the yields of gasoline fractions from crude oil. The first new "cracking" process made its appearance in 1912. As far back as 1792 cracking, which is a process to convert hydrocarbons with high molecular weights and boiling points into hydrocarbons with lower molecular weights and boiling points, was used in England for the manufacture of illuminating gas. The first practical process for the production of motor fuel was, however, introduced by Dr. William Burton of the Standard Oil Company of Indiana in 1912. In the Burton cracking process a heavy gas oil or similar material was charged into a horizontal coal-fired still. The temperature was raised and the pressure was maintained while the gases evolved slowly from the heated oil. The resulting yield of 35% gasoline was a significant improvement over the simpler "skimming" methods in use at the time. By 1918 about 3% of the total gasoline production in the U. S. was made by cracking processes, and by 1921 there were over 2000 Burton stills in operation.

With cracking large quantities of easily oxidizable unsaturated compounds were produced. These fuels, when stored, formed deposits of resinous gummy materials in refinery tanks and pipe lines, and the valve stems, fuel lines, and carburetors of engines. Although the copper dish method for the detection of corrosive sulfur compounds and gum-forming materials was a

part of aviation gasoline specifications during World War I, this test was not adequate for cracked fuels. Since there was no reliable method for measurement of gum-forming compounds, aviation gasoline specifications severely limited the quantity of cracked stocks that could be blended in. U. S. Government specifications for gasoline, prepared in 1922 by a committee of various engineering societies were the first to control corrosion and gumming by limiting the inclusion of cracked stocks. The fact that cracked gasoline had better anti-knock properties was not appreciated at first, so for many years aviation gasoline, unless blended with benzol, was poorer in detonation performance than motor gasoline.

Air cooled engines, development of which started in the early 1920's, were responsible for revealing the great shortcomings of aviation gasoline and the need for better anti-knock properties. Charles Lawrance designed a series of engines for the Wright Aeronautical Corporation. The detonation and overheating problems of these engines led to increasing use of tetraethyl lead (TEL) in the fuel. The U. S. Navy became the first service in 1926 to use fuel containing TEL. They carried cans of TEL fluid in the aircraft and added it to the tanks when refueling. This hazardous procedure continued until 1933.

Investigations started about 1929 by the Power Plant Laboratory at Wright Field under the direction of Samuel D. Heron showed that use of benzol as a means to increase the anti-knock value of gasoline was largely ineffective in air cooled radial engines. This was especially the case with the models which were then being introduced with more efficient superchargers to increase takeoff horsepower and altitude performance. The higher the temperature of the fuel/air charge, especially at lean mixture conditions, the less effective benzol became. The Wright Field tests showed, however, that TEL was a highly effective anti-detonant in air-cooled engines. The outcome of these investigations was that in 1930 the U. S. Army Air Corps specified a minimum octane requirement of 87, the first specification for aviation gasoline to include an octane number requirement. The octane requirement of 87 necessitated the use of TEL; a maximum of 3 cc/U. S. gallon being permitted.

The introduction of 87 octane fuel encouraged the development of improvements in aircraft engines that could be realized by the use of fuels of higher anti-knock value. The 1930's witnessed a rapid advance in the development of gear driven superchargers. The resulting increases in the density and temperature of the fuel/air charge necessitated fuels of still higher octane number. The quest was on to produce high octane fuels economically. Petroleum research in the early 1930's clearly showed hydrogenation to be the most effective process for converting the heavier fractions of petroleum into gasolines with much higher octane numbers than those that could be obtained by straight run distillation of selected crudes. High pressure hydrogenation had originally been developed in oil short Germany during the 1920's as a means for converting coal into liquid hydrocarbons. In the U. S., Standard Oil of Louisiana began, in the late 1920's, an intensive program to develop high pressure hydrogenation processing techniques to improve the quality of products refined from Texas crudes. The first gasolines produced by high pressure hydrogenation were not satisfactory as blending components for aviation gasoline, because of instability in storage and poor anti-knock performance. However, subsequent work soon led to the discovery of catalysts which allowed conversion of low grade aromatic kerosenes and gas oils into highly stable aviation gasolines with relatively high octane numbers. (This process is now known as hydrocracking.) Blends of the hydrogenates with isopentane to adjust volatility, and 3cc TEL/gallon resulted in 92 octane aviation gasoline of excellent quality.

S. D. Heron's program of full scale engine testing of fuels, that he began at Wright Field in 1929, played a major role in convincing the Air Corps and engine manufacturers of the gains in power output and efficiency that could be achieved with fuels of higher octane number. Early tests demonstrated that 92 octane fuel permitted an increase of 30 to 35% in takeoff power, as compared with the unleaded gasoline of 50 to 60 octane number formerly in use. Tests conducted with a Pratt & Whitney Wasp R-1340 engine with a maximum takeoff power of 720 horsepower (when fueled with 92 octane fuel) showed that 900 horsepower could be obtained with a 98 octane fuel containing 8 cc TEL/gallon. The first experimental specification for 100 octane fuel, designated X-3575, was issued by the Army Air Corps on February 1, 1934. The Wright Field fuel testing that led to the Army setting its sights on 100 octane gasoline was reported at the Third Annual Meeting of the Institute of the Aeronautical Sciences in January, 1935 by F. D. Klein, an Air Corps pilot who, following a flying accident, became assistant to S. D. Heron. His paper was entitled "Aircraft Engine Performance with 100 Octane Fuel". The publication of the Klein paper was the milestone which marked the introduction of 100 octane aviation gasoline in the U. S.; first for military aviation, and then within 10 years as the standard grade for commercial aviation. Procurement by the Army Air Corps of substantial quantities of 100 octane gasoline stimulated some of the major oil companies to conduct vigorous research and development of methods for manufacturing iso-octane blending agents at reasonable cost. One of the first commercially successful blending agents was "hydrocodimer". This was manufactured from refinery gases in a two step operation consisting of polymerization, in the presence of sulfuric or phosphoric acid, of isobutylene and normal butylene to form trimethyl pentanes, followed by hydrogenation of the pentenes to give a mixture of iso-octane and other isometric octanes. A major breakthrough in the development of refinery processes for the manufacture of iso-octane occurred in 1937 with the advent of the alkylation process. Alkylation may be considered a special case of polymerization in which an olefin, such as isobutylene is united with a paraffin, such as isobutane, to form a heavier and saturated hydrocarbon, eg., iso-octane. During the period 1935-37, several oil companies, working independently, made important progress toward the commercial application of the alkylation process. The first commercial plant went of stream at Humble's Baytown refinery in 1938.

By 1938 about 90% of U. S. government fuel purchases were of the 100 octane grade which had become the principal fuel used by the Army Air Corps. In Britain 87 octane gasoline was the standard fuel used for the bomber and fighter aircraft of the Royal Air Force. There was considerable soul searching in Britain on the question of whether the engines of the RAF aircraft should be developed to use 100 octane instead of 87 octane. Many authorities maintained that, in the event of war, the 100 octane fuel,

which at that time was produced only in the U. S., could be unavailable to Britain. Fortunately for Britain and the RAF, which was to be engaged in mortal combat with the German Luftwaffe only three years later, those authorities went unheeded. Beginning in 1937, the development of engines to use 100 octane fuel was given full support by the Air Ministry's Director of Technical Development.

The Merlin powered Hurricanes and Spitfires of the Royal Air Force were in a standoff with the German Messerschmidt 109E with its Daimler-Benz 601A engine at the outbreak of war in 1939. The British aircraft were faster but the German plane climbed more rapidly. The availability of 100 octane fuel in April 1940 made it possible to increase the Merlin's intake manifold pressure from 42 to 54 inches of mercury, and to increase its combat rating from 1030 to 1310 horsepower. This vital improvement made possible the better climb and speed performance of RAF fighters that enabled them, three months later, to win the Battle of Britain in the skies. The war in Europe greatly increased the need for 100 octane fuel. By mid-1940 it was being produced by U. S. refineries at the rate of 650,000 gallons/day. This increased to 1.25 million gallons/day by the end of 1940. Much of this was shipped to Britain. Over 80% of the 100 octane fuel consumed by the RAF during the Battle of Britain came from U. S. refineries. When, in May 1940, President Roosevelt announced a plan to build a 50,000 airplane Air Corps, intensive studies began into the problem of producing the tremendous quantities of 100 octane fuel that would be necessary. While conventional thermally cracked gasoline was unsuitable as an aviation gasoline component, it became evident that it would be essential to use catalytically cracked material as the base gasoline required for blending with the alkylate. The original catalytic cracking processes developed by Eugene Houdry in France in the 1920's. Houdry came to the U. S. in the 1930's and continued development of his process in collaboration with the Socony-Vacuum Oil Co. and the Sun Oil Company. A second catalytic cracking process was developed by the Standard Oil Development Co. in technical collaboration with other industry members. It employed a fluidized catalytic bed that permitted continuous operation without a need to shut down the unit for catalytic regeneration. These methods enabled staggering increases in fuel production that were needed for the war effort. By December 1942, production of 100 octane gasoline had risen to 5.5 million gallons/day; by June 1943, it was approaching 10 million gallons/day; and, by VE-Day, May 7, 1945, production exceeded 20 million gallons/day.

When the U. S. 100 octane fuel was adopted by the RAF in 1940, a rich mixture rating was called for since the British discovered that batches of octane fuel varied in their rich performance. They required that 100 octane fuel meet the performance of iso-octane containing 1 cc TEL/U. S. gallon when tested in a supercharged engine under rich mixture conditions. This comparison with leaded iso-octane subsequently became the basis of the Performance Number scale. Of the various hydrocarbon types, aromatics clearly had the best rich mixture performance, presumably because of their stability at high temperatures. early in 1942, a similar rich mixture requirement was specified by the U. S. Army. The grade became known as 100/125. The rich rating was slightly upgraded shortly thereafter to the equivalent of iso-octane plus 1.25 cc TEL/gallon. The grade was then designated 100/130. The number "130" was based on a Performance Number (PN) scale that assumed a 100 PN fuel would match unleaded iso-octane in a supercharged engine, while a 130 PN fuel would permit 130% of the power available from iso-octane alone.

As larger and longer range aircraft such as the Boeing B-29 were designed, the Air Corps and the Navy, encouraged by the engine manufacturers, began to show interest in still higher knock ratings than 100/130. In July 1944, Specification AN-F-33 was issued for Grade 115/145 aviation gasoline with a TEL content of 4.6 cc/gallon. Manufacture of the Grade 115/145 fuel required almost double the amount of alkylate in the blend, so production of Grade 115/145 involved the sacrifice of nearly two gallons of Grade 100/130. For this reason, use of Grade 115/145 was delayed until about the time of VE-Day. At the conclusion of the war, the demand for aviation fuel began to slacken. Nevertheless, all the gasoline plants were kept in operation although their output was reduced as a result of production of Grade 115/145 and reduction of the TEL content of Grade 100/130 from 4.6 to 4.0 cc/gallon. In 1946 the lead content of Grade 100/130 was further reduced to 3 cc/gallon. By 1947, the free world demand for aviation gasoline had shrunk from its 1945 record volume of over 26 million gallons/day to less than 5 million gallons/day. At that time many of the alkylation plants built in the 1940-44 period had been shut down, or diverted to production of premium motor gasoline. Likewise most of the production of the catalytic cracking plants had been diverted to motor gasoline. The start of the Cold War and the Berlin Airlift (June 1948-May 1949), and on June 25, 1950 the start of the Korean conflict created a significant increase in the need for Grade 100/130 and Grade 115/145 aviation gasoline. At the same time commercial use of aviation gasoline was increasing at a rate of 15% each year. The Department of the Interior in order to increase production capability directed that TEL content of the 100/130 grade be raised to 4.6 cc/gallon from the 3 cc level preferred by the airline operators. A waiver was granted in the case of Grade 108/135 which was allowed to remain at 3 cc/gallon. The Grade 108/135 was a new grade introduced in 1949 for the Pratt & Whitney 3500 horsepower R-4360 Wasp Major engine and certain models of the R-2800 Double Wasp engine, which had previously been rated on Grade 115/145. The high lead content (4.6 cc TEL/gallon) caused difficulties in airline operations due to spark plug fouling and exhaust valve burning. With the same base stock used for Grade 115/145, reducing the TEL level to 3 cc/gallon lowered the lean and rich performance numbers to 108 and 136. The introduction of Grade 108/135 in 1949 was the last chapter in the technical development history of aviation gasolines. The availability of Grade 108/135 was phased out many years ago, but Grades 100/130 and 115/145 are still available for the portion of the aviation industry still using piston engines.

C. TURBINE ENGINE FUELS

The principle of the gas turbine engine is as old as the Otto cycle engine, and a successful turbine engine with a continuous combustion system had been developed in France by 1906. Because of its low efficiency, the principal application of the gas

turbine during the following 30 years was in blast furnaces. They were used as turbo-blowers to extract otherwise wasted heat energy from the furnace gases to provide high pressure air to the furnace. The idea of utilizing the energy in a hot exhaust gas for propulsion is of ancient origin. The reaction principle had been recognized by rocket builders for many centuries. The concept of using the exhaust of a reciprocating engine for aircraft propulsion was, in fact, proposed by the Frenchman Rene Lorin in 1908. The use of the exhaust of a gas turbine for jet propulsion was patented by another Frenchman, M. Guillaume, in 1921. The turbo supercharger, which was first tested in 1911, and flown in aircraft engines as early as 1916, directed the engine exhaust to a turbine which drove an air compressor. Studies of the gas turbine as a primary aircraft power plant carried out in both Britain and the U. S. after World War I, concluded that the most efficient jet engine conceivable would have a much higher fuel consumption than a reciprocating engine and generate much less power/ pound of weight. These early (and erroneous) estimates were based on the technology then existing for industrial turbines, and failed to recognize any possibility of light weight construction. None of these early studies considered that the simpler fuel requirements of a gas turbine represented an important incentive for its development.

An explanation for the slow development of the aircraft gas turbine engine lay in the failure to think in terms of truly high speed aircraft. Flying Officer Frank Whittle in Britain had a primary interest in the aerodynamic advances that had been made during the 1920's. His analysis, in 1928, of B. M. Jones paper on drag due to turbulence led him to conclude that streamlining an aircraft would make higher speeds possible and reaction propulsion much more efficient. He thought in terms of a 500 mph aircraft, operating at very high altitude. At those conditions, everything was in favor of a jet engine; the high speed would assist the compressor, and the low temperature of high altitude would improve thermal efficiency. Whittle also envisioned utilizing power directly as exhaust thrust, rather than taking it through heavy gearing to a high drag propeller. His 1930 patent, while not the first in the field of gas turbines, represents the first practical concept for its application to aircraft. It formed the basis for subsequent development of jet engines in both Britain and Germany. From the beginning, Whittle realized that the combustion system would be a critical component. He turned to experts in oil burners for help with combustor design. The first tests of Whittle's WU engine in April 1937 revealed serious problems in combustion of the kerosene that was fed to a single chamber. By October 1938 when the third engine was tested, the single chamber had been replaced by ten individual chambers that made it possible to study combustion phenomena in one chamber with modest blower capacities. Combustion in a turbine engine is more analogous to a furnace than it is to the intermittent ignition of compressed fuel/air mixtures in a cylinder. To cope with the much higher heat release rates, it is necessary to use excess air to cool the walls and mix with the combustion products before they pass through the turbine. The principal problem in combustor design is skillful air management, dividing the compressed air stream so that a small portion aids atomization and mixing, while the bulk cools the walls and mixes with the combustion products to establish a uniform temperature hot gas stream for expansion. All of this must be done continuously with minimum pressure drop, using high pressure air, moving at high subsonic velocities. Moreover, the combustor must be capable of handling large excursions in fuel and air flows as the thrust is varied between idle, taxi, takeoff, climb, and cruise settings. It is not surprising that the combustor became the most critical design item in the first turbojet engines. At the same time, defining combustion properties of jet fuels became just as important as the anti-knock values of gasoline.

The second turbojet engine pioneer, Hans von Ohain in Germany, was a student in Goettingen in 1935 when he first developed an interest in the technology. His engine, unlike Whittle's, had a combustion system outside, rather than behind, the compressor. Von Ohain was hired by Ernst Heinkel, an aircraft builder, who was farsighted about high speed aircraft and the potential for jet propulsion. The first demonstration engine run was in March of 1937, one month before the Whittle engine ran in England. Due to the success of von Ohain's engine, design of a flight engine began immediately. To avoid problems anticipated with combustion of liquid fuels, von Ohain's first engine was designed to burn gaseous hydrogen. The combustor of the flight test engine proved to be a problem, so a redesigned engine, known as the Heinkel S-3b, burned liquid fuel. This engine was installed in the Heinkel 178 aircraft, which made the world's first turbojet powered flight on August 27, 1939, using aviation gasoline as the fuel. The British were unaware of this, and it was nearly two years later (May 15, 1941) when the Whittle engine flew in the Gloster Meteor aircraft. Despite their head start in turbojet engine development, Germany did not decide until 1943 to devote a major portion of their dwindling resources to jet fighter production. One of the arguments for development at that time was Germany's shortage of high octane fuel and the fact that the jet engine could run on diesel fuel. Germany produced about 5000 Junkers 004B engines, which were used in 1400 twin-jet Messerschmidt 262 fighters. These fighters began in service in August 1944 and proved to be nearly 100 mph faster than Britain's jet powered Meteor I, which had entered service the month before. The impressive results displayed by the Me 262, in the destruction of slower American bombers struck a note of real alarm among the Allies.

In the U. S., as in Europe, early thinking about the gas turbine engine was dominated by the assumption that it would be used to drive a propeller. It was 1939 before a careful General Electric study concluded that a turbojet would be a superior utilization of the technology, and that it would show its superiority at high speeds of about 500 mph. In March of 1941, General Hap Arnold, who had seen the Whittle engine, requested that the NACA establish its Special Committee on Jet Propulsion. Preliminary studies were so promising that contracts were awarded to three companies: Allis-Chalmers, Westinghouse, and General Electric. General Electric, builder of turbo-superchargers, tested its version of the Whittle engine, called the I-A in March 1942. Two of these engines flew on Oct 2, 1942 in Bell's P-5A aircraft, to launch the U. S. into the jet age. The need for more powerful engines became apparent with the first test flights in England and the United States, because the aircraft could not achieve the speeds or fuel economies desired. The British built the de Havilland Goblin with 3000 pounds of thrust, and in the U. S. the GE I-40 (later designated as the J-33) developed 4000 pounds of thrust. Britain, however, led in the development of turbojet engines

until the end of the war, mainly because the U. S. choose not to divert the major engine builders: Pratt & Whitney, Curtis Wright, and Allison, from their primary task of producing large piston engines.

Most of the jet engines developed before the end of World War II utilized ordinary kerosene as a fuel. Whittle had considered diesel fuel, but kerosene was chosen for flight testing because of its low freeze point. The NACA Fuels Subcommittee first discussed fuels for jet aircraft in September 1944. The Navy, at that time, indicated an intention to use aviation gasoline in jet engines to simplify fuel supply aboard aircraft carriers. Concerned with the potential availability of kerosene, the NACA committee, in March 1945, asked the Bureau of Mines to explore the physical and chemical characteristics of crude fractions boiling between 150°F to 600°F. In Britain, consideration was given to a fuel specification shortly after the first flight of the Gloster Meteor. Specification RDE/F/KER/210, issued in 1943, described a conventional lamp burning kerosene with -40°F freeze point. In the U. S. the first jet fuel specification was AN-F-32a, issued in April, 1944. This was subsequently labelled JP-1 under MIL-F-5616 in 1950. It described a typical household kerosene of 110°F flash point, but required a -76°F freeze point, the same as aviation gasoline. The stringent freeze point requirement effectively limited JP-1 availability to about 3% of the crude oil supplies. In 1945 the Army proposed a wide cut fuel (designated AN-F-34, and later JP-2), with the hope of expanding supplies. However, the use of JP-2 was limited to experimental testing and experimental service use because its viscosity was unsuitable, and the potential hazard of a flammable vapor space between 20 and 80°F at sea level.

In 1946 the NACA Subcommittee on Aircraft Fuels proposed that two prototype fuels be evaluated. Fuel A combined the volatility of aviation gasoline and kerosene, and Fuel B was a 100°F flash point kerosene similar to JP-1. Availability of Fuel A as a percent of crude was 48%. For Fuel B it was 13%. Prototype A became AN-F-58a in 1947, and was subsequently labeled JP-3 when MIL-F-5624 was issued in 1950. Low volatility had been a problem for early jet engines burning kerosene because above 30,000 feet at low engine powers it was difficult to maintain stable combustion. Blowouts and relighting difficulties were found to be more prevalent with JP-1 than with aviation gasoline. However, with JP-3 (and aviation gasoline as well), the high volatility caused fuel boil off losses and vapor lock, particularly at a high rate of climb. A 1950 Navy supported study established that entrainment losses, which were several times larger than evaporation losses, were much greater for JP-3 than for aviation gasoline when climbing to 60,000 feet at 10,000 feet/minute. A large quantity of foam formed with JP-3. On the other hand, no losses were observed with JP-1. The entrainment was due to supersaturation of fuel tank air which would release suddenly to generate foam. Various techniques for coping with high vapor pressure JP-3 were considered. Tank pressurization, fuel pre-cooling, and other means were considered, but each involved serious weight penalties or complex handling problems. Finally it was decided to alter the distillation fraction by lowering the maximum Reid vapor pressure from 7 to 3 psia, thus reducing evaporation losses at high altitude to a very low level. This wide cut fuel, labeled JP-4, was standardized under MIL-F-5624A, which was issued in May 1951.

During the distillation of crude oil to make JP-3 or JP-4, a wide cut is taken of the distillate so as to include both the naphtha (gasoline) and kerosene fractions. JP-4 is typically composed of about 50 to 60% gasoline, and the remainder is kerosene. The primary advantage of the wide cut is the greatly increased availability of the resulting fuel. In 1951, up to 60% of a barrel of crude oil could be converted into JP-3, or about 40% into JP-4. These estimates were based on the use of high quality, light crude oils that have not been available in quantity for many years, and on the inclusion of cracked components. These yields per barrel have been decreased somewhat as a result of the limit on cracked products (olefins), and on the heavier, lower quality crude oils that are normally available today.

The U. S. Navy used aviation gasoline, because of its shipboard availability, to fuel its first carrier-based turbojet aircraft. It was soon learned, however, that the lead in the fuel was attacking the engine hot section components. One approach suggested was to blend the aviation gasoline with a kerosene fuel to form "Jet Mix", a product similar to JP-4. JP-5, a high flash point kerosene developed by the Navy for use in Jet Mix, was first covered by specification MIL-F-7914, dated March 11, 1952. Subsequently, JP-5 was included in MIL-F-5624B, dated December 7, 1953. Although considerable development work was done on Jet Mix, this product was not used operationally. The Navy found that their aircraft flew very well on straight JP-5. JP-5 has a minimum flash point of 140°F, and is used for shipboard safety reasons. To maximize availability of this fuel, the Navy selected a maximum freeze point of -50°F. For ship launched aircraft this has been found to be adequate, as they fly relatively short duration missions, and the thermal mass of the oceans tends to prevent the extremely low surface temperature conditions that may occur over land.

The first supersonic flight was made on October 14, 1947 in the Bell X-1 rocket powered research airplane, but it was not until 1949 that a jet engine powered research aircraft, the Douglas D-558-II Skyrocket, first exceeded the speed of sound. The first service supersonic fighter, the YF-100A, powered by the Pratt & Whitney J-57 engine, flew in 1953. In 1956 the B-58 was the first bomber to fly supersonically. These aircraft achieved supersonic flight through operation of the jet engine afterburner. Because of the enormous fuel usage rate, the duration of supersonic operation was very limited. As a result, it was possible to use JP-4 fuel, since the heating effect of ram air did not raise the temperature of the fuel to the point of boil-off. The B-70 bomber was initially planned as a user of high energy borane slurry fuel, but when the exotic fuels research program was cancelled in 1963, the Air Force looked to a conventional fuel with a sufficiently low vapor pressure to avoid boil-off during long duration supersonic flight. MIL-F-25656 for JP-6 was issued in 1956. JP-6 was a kerosene based fuel similar to JP-5, but with a lower freeze point and improved thermal stability. JP-6's vapor pressure of .5 psi at 100°F was considerably lower than the 3 psi of JP-4. It was estimated that JP-6 availability might be 30% that of JP-4. This cast severe doubts on the possibility of

converting the entire Air Force to the new fuel. The cancellation of the XB-70 program eventually led to the cancellation of the JP-6 specification.

For the U-2 aircraft, flying at extremely high altitudes, yet another special purpose fuel was required. JPTS is the kerosene fuel that was developed specifically for the J57 engine used in the U-2. It featured a low freeze point, and improved thermal oxidative stability. The early test fuel for the U-2 was identified as LF-1, being essentially a paraffinic kerosene used as commercial lighter fluid. MIL-T-25524 for JPTS (Thermally Stable Jet Fuel) was issued in 1956. The thermal oxidative stability of early production batches of JPTS often degraded during short term storage. Two changes were made to the specification in order to avoid this problem. First, the thermal oxidative stability requirement was increased for purchase of the fuel, while retaining the former requirement as the operational use limit; and secondly, a proprietary additive, JFA-5 (Jet Fuel Additive 5), produced by the DuPont Company, was added to all JPTS fuel.

The SR-71 aircraft, which was developed in the 1960's, cruises at Mach 3+, at very high altitude. Its development required a new fuel, designated JP-7, having a low vapor pressure and excellent thermal oxidative stability. To insure adequate combustor life, the fuel was also required to have excellent combustion characteristics, and a high net heat of combustion. The requirements essentially limited the composition of JP-7 to paraffins and cycloparaffins. The aromatic content is typically below 3 percent by volume. This composition results in a fuel with a relatively high freeze point of -46°F. This is not a problem because the supersonic cruise speed of the SR-71 provides aerodynamic heating for the fuel tanks. JP-7 is not a distillate fuel, as are the other jet fuels. It is composed of special blending stocks that have been subjected to special processes to remove the aromatics. This special processing results in a very clean hydrocarbon mixture that is very low in the sulphur, nitrogen, and oxygen impurities normally found in distillate fuels. As a result, JP-7 has excellent thermal oxidative stability, but very poor lubricating properties. A special fuel lubricity additive is used in JP-7 to prevent excessive wear of the engine fuel pump. The specification for JP-7, MIL-T-38219, "Turbine Fuel, Low Volatility, JP-7", was issued in 1970.

Combat experience, observed during the Vietnam War, revealed that the U. S. Air Force aircraft, using highly volatile JP-4, had higher combat losses than U. S. Navy aircraft, using lower volatility JP-5. Also, crash data indicated that the probability of a post crash fire is nearly 100% when using JP-4; much higher than with a kerosene fuel such as JP-5 or commercial Jet A. The superior safety of kerosene fuels, as compared to wide-cut fuels, such as JP-4, was also evident in the number and severity of ground handling accidents. JP-8 was developed to provide a safer, kerosene based jet fuel (similar to commercial Jet A-1) for the Air Force. It was developed to have adequate availability and an acceptable freeze point (initially -50°C, but subsequently changed to -47°C). The initial specification for JP-8, MIL-T-83133) was issued in 1976. Conversion from JP-4 to JP-8 was begun in 1979, and completed in 1994. U. S. Air Force operations in Great Britain were the first to employ JP-8 as the primary turbine engine fuel. The use of JP-8 soon spread to all U. S. Air Force operations in Europe, but conversion of the continental United States, and the rest of U. S. operations worldwide was slowed as a result of concerns regarding availability, low temperature operations, and materials compatibility. In an effort to simplify supply operations, the U. S. Army has also converted its ground vehicles (tanks, trucks, etc.), and equipment (heaters, generators, etc.), as well as its airplane and helicopters to run on JP-8 fuel. This has made JP-8 the single fuel for battlefield use. The U. S. Navy still retains JP-5, however, as the shipboard fuel of choice.

The petroleum shortages in the United States, resulting from the Arab oil embargo of 1973, pointed out the need for an assured domestic source of jet fuel. The coal reserves of Pennsylvania and other regions of the U. S., and the oil bearing shale rocks of the Rocky Mountain area are an almost limitless potential source for turbine engine fuels, as well as other products ordinarily produced from petroleum. The tar sands of Canada are also an easily accessible source of similar promise. The use of alternative source synthetic fuels has been limited by the relatively low cost and generally adequate availability of petroleum, but the technology for producing synthetic fuels is in hand. In the 1980s, a program was initiated to demonstrate the suitability of shale derived JP-4 for U. S. Air Force use. Engine testing and flight demonstrations indicated no deleterious effects resulting from the use of shale derived fuel. This program provided assurance that the JP-4 specification is restrictive enough to ensure that the fuel is adequate, regardless of the source, as long as all of the specification requirements are met.

The Integrated High Performance Turbine Engine Technology (IHPTET) initiative is a joint Air Force, Navy, and Army program to double turbine engine performance (in terms of thrust to weight ratio) by 2002. It is a three phase program with incremental goals for performance improvement in a number of categories in addition to thrust to weight ratio. To improve the basic parameter of thrust to weight ratio, there are two approaches that can be taken. First, you can reduce the weight by using improved materials and structural concepts; and second, you can increase thrust. To increase thrust for a given engine, you can increase the temperatures in the engine by increasing the amount of compression, which increases the temperature of the air entering the combustor, and you can use a larger percentage of the air for burning fuel, and less for cooling combustor walls. This not only puts a significant burden on the structural members of the engine, but also creates a severe environment for the fuel entering the engine.

At high temperatures the fuel tends to become unstable and precipitates carbeneous materials. Oxygen dissolved in the fuel reacts with other fuel components to form additional carbeneous material. The carbon deposits on the walls of fuel lines and manifolds, and can be particularly damaging for fuel nozzles, valves, and other fuel control elements. Fuel system and engine designers generally try to restrict the temperature of the fuel to a maximum of 325°F at the point at which it enters the combustion chamber, the fuel nozzle. This design practice has generally proven to be adequate, and operational problems have

been relatively rare. A great deal of maintenance, however, has been required to periodically clean or replace fuel system components because of carbon deposits. For high performance special use aircraft, such as the U-2 and the SR-71, the problem has been avoided by the use of specialty fuels (JPTS and JP-7). The use of the specialty fuels, however, creates severe logistical problems, which limits the operational utility of the aircraft. The cost of the specialty fuels and their availability makes conversion of the entire fleet to one of these fuels impractical.

In order to meet the needs of advanced aircraft using engines derived from the IHPTET initiative and to reduce overall fuel system maintenance costs, the Air Force has developed a fuel designated JP-8+100. JP-8+100 is not a new fuel, but simply JP-8 with additional additives to increase the thermal stability limit of the fuel by 100°F, from 325°F to 425°F. The thermal stability is the limiting factor in how much heat can be absorbed into the fuel. JP-8+100 will potentially allow up to 50% more heat to be absorbed without breaking down into carbon, tars and gums which are the primary causes of fuel system contamination.

Even with existing aircraft, there are conditions where the fuel used by the engines is insufficient for the heat loads desired. Some airframe designers have used a technique called 'recycling' to meet their thermal management needs. In certain flight situations, more fuel is drawn than what the engines can use to prevent the current 325 °F temperature limit from being exceeded. The excess is recycled back to the fuel tanks. Unfortunately, the fuel (JP-8) suffers some loss of thermal stability after being heated to its limit. This causes the buildup of soluble carbon, gums, tars and other materials throughout the fuel system and causes an increased rate of breakdown of the fuel when the fuel is recycled subsequent times. The increased thermal stability of JP-8+100 nearly totally eliminates any thermal stability breakdown problems when recycled at 325°F, potentially keeping the fuel systems of even the most advanced aircraft clean compared to standard JP-8.

The additional additive package in JP-8+100 is comprised of three components: one to act as a dispersant, to keep in suspension, and off the walls, any carbonaceous material that is formed in the fuel; another to act as a detergent to clean deposits off the walls as they are forming; and a third to act as an anti-oxidant to keep the dissolved oxygen in the fuel from reacting with other components in the fuel. JP-8+100 has undergone extensive scientific testing in U.S.A.F facilities, engine ground testing, and is currently undergoing flight testing at several locations. The goal is to replace JP-8 at a cost penalty of less than .1 cents/gallon of fuel, which will be more than offset by the reduction in maintenance costs in existing aircraft. Future aircraft will be designed to take advantage of the higher possible heat sink, enabling higher performing aircraft and fuel systems.

Endothermic fuels are fuels that contain molecules that can be cracked to smaller molecules, with or without a catalyst, and in the process absorb heat. For high Mach number high performance aircraft, the generation of excess heat can be a monumental problem and endothermic fuels are very attractive. The Air Force and other agencies have done extensive work in characterizing methylcyclohexane (MCH) and other hydrocarbons for endothermic fuel use.

D. FUEL SPECIFICATION REQUIREMENTS AND TEST METHODS

Testing has been an integral part of fuel specifications since issuance in 1907 of the first United States Government specification for the purchase of gasoline. Specifications are written to ensure that the important properties of a product vary only to the extent that the variations will have no deleterious effect on its performance in its intended use. Devising tests to enable fuel purchasers to determine whether or not that goal of the specifications is being met has been a continuing challenge. The 1907 specification required only that the fuel be of a certain specific gravity, and that it not be contaminated with materials that would be left as a residue after the gasoline has been vaporized. As the demands on fuel grew greater, the scope of the specifications increased to include limits on chemical makeup, as well as more physical performance requirements. By 1922 there were standard tests established for color (Saybolt Number), corrosion and gums (copper dish test), and sulphur content (Doctor test), as well as others. Testing for Octane number became a major focus, starting in 1930. For high altitude use, the freeze point became an important parameter to be evaluated. The American Society of Testing and Materials (ASTM) has been a powerful force in the development and standardization of test methods for fuel specification testing.

For current fuels used by the Air Force, the specification requirements can be broken into three categories: chemical composition, physical properties, and miscellaneous requirements. The first category includes tests to determine the hydrocarbon types in the fuel, to evaluate the sulphur and mercaptan sulphur content and to quantify the organic and inorganic acids in the fuel. Physical properties include density (or specific gravity), volatility, vapor pressure, flashpoint, viscosity, and freeze point. Miscellaneous requirements include determination of combustion performance, burning quality, corrosivity, cleanliness, particulates, thermal stability, color, existent gum, and electrical conductivity.

The aromatic and olefin content of a fuel are important chemical composition parameters. Aromatics have the poorest combustion performance of the four major hydrocarbon types found in jet fuels (paraffins, cycloparaffins, olefins, and aromatics), and also are excellent solvents. The elastomers used in aircraft fuel systems for sealants, gaskets, and hoses can be adversely effected if the fuel aromatic content is not controlled. Olefins are the least stable of the hydrocarbons types in fuel. Petroleum products that have appreciable concentrations of olefins tend to polymerize, forming gums during storage. A maximum olefin content of 5% is specified for most jet fuels in order to help prevent the formation of gums and resins.

ASTM D1319 "Tests for Hydrocarbon Types in Liquid Petroleum Products by Florescent Indicator Adsorption" specified the accepted method for measuring the volumetric concentrations of aromatic and olefin hydrocarbons through liquid

chromatography. Fluorescent dyes are added to the fuel before the fuel is injected into a glass column packed with silica gel. Alcohol is injected into the column after the fuel. This separates the hydrocarbon types within the column according to their adsorption affinities. The fluorescent dyes, preferentially adsorbed by the hydrocarbon types, enable the quantities of aromatics and olefins to be measured when the glass column is illuminated with ultra-violet light.

Bromine Number can be used to measure the olefin content of a fuel. Bromine readily reacts with olefins at ambient temperature, so the amount of bromine consumed by a specific quantity of fuel determines the olefin content. Jet fuels tend to naturally have olefin contents well below the specification limits, and the Bromine Number test was dropped from the specification for JP-4 and JP-5 in 1962. The apparent intent of the limit on olefins was to prevent the addition of cracked stocks to jet fuels. Jet fuel production capability has been adequate to meet the needs without using cracked products, thus far. If cracked products are eventually used in jet fuels, hydrogenation can be used to convert the unstable olefins to stable paraffins, but at an increase in cost.

Organic compounds containing sulphur are commonly found in fossil fuels, including petroleum. The total sulphur content may range from a few parts per million to several percent, and may include sulfides, disulfides, sulfones, sulfuric acids, sulfoxides, thiophenes, and mercaptans. Some sulphur compounds are highly corrosive even before combustion, but combustion converts all sulfur compounds to sulfur dioxide, which, in the presence of air and water reacts to form sulfuric acid, which is highly corrosive. Military jet fuel specifications limit total sulfur content to .3 to .4 percent in order to reduce corrosion problems in engines. Mercaptan sulfurs, which are characterized by their strong, noxious odor, are even more limited, as they are highly corrosive, and they can degrade some aircraft fuel system elastomers. Mercaptan sulfurs are generally limited to .002 or .003 percent by weight. Mercaptan concentrations may be measured directly by using ASTM D 3227 "Test for Mercaptan Sulfur in Gasolines, Kerosine, Aviation Turbine and Distillate Fuels (Potentiometer Method)", or indirectly through use of the Doctor Test, described in ASTM D 235, "Standard Specification for Mineral Spirits".

Organic acids and traces of inorganic acids, left in jet fuel following refining, can corrode aircraft fuel system components, and some organic acids can emulsify water in fuel and react with dissolved metals in water bottoms to form filter-plugging precipitates. The Total Acid Number specification limit in jet fuels is .015 mg/gallon of fuel, which is adequate to avoid fuel system problems.

The density of a jet fuel is one of the parameters that controls the composition and other physical properties. Density is normally measured as specified in ASTM D 1298, "Test for Density, Specific Gravity, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method". (A hydrometer is a calibrated float whose displacement can be directly related to density.) Current fuel specification density limits are based on fuels composed of about 20 to 40% cycloparaffins, 10 to 20% aromatics, and the remainder paraffins. Aromatics are the most dense, then the cycloparaffins and the paraffins which are the least dense. Fuel density must be known for the pilot to accurately calculate the mass of his fuel load, as fuel is generally serviced volumetrically. Fuel controls also meter fuel volumetrically, so adjustments must be made to compensate for density differences.

Volatility is the tendency of a liquid to vaporize, or to change from a liquid to a gas. Hydrocarbon fuels burn in the gaseous state only, so, for engine starting, jet fuels must be sufficiently volatile for part of the fuel to vaporize prior to ignition. Control of fuel volatility is achieved by limiting the fuel vapor temperatures during separation by distillation. The distillation characteristics of a fuel can be determined by evaporating the fuel and recondensing the vapors in a graduate, while simultaneously measuring the vapor temperature and volume of condensate recovered. Distillation test methods include ASTM D 86, "Test for Distillation of Petroleum Products", and ASTM D 2887, "Test for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography".

The vapor pressure of a jet fuel is a direct method for specifying volatility. ASTM D 323, "Vapor Pressure of Petroleum Products, Reid Method". or ASTM D 2551, "Test for Vapor Pressure of Petroleum Products (Micromethod)" can be used to determine vapor pressure. In these methods, a specified amount of the fuel is placed in a pressure container. The container and contents are heated to 37.8°C and the pressure increase is recorded. This pressure rise is the Reid Vapor Pressure.

Kerosene fuels such as JP-5 and JP-8 have vapor pressures that are an order of magnitude less than that of JP-4. The simple vapor pressure tests are not suitable for these fuels, so the temperature at which the fuel can be heated so as to just produce sufficient vapor to flash is measured. As the amount of fuel vaporized is directly related to its vapor pressure, the flash point is an indirect measure of the volatility of the fuel. Flashpoint test methods commonly specified include: ASTM D 56, "Test for Flash Point by Tag Closed Tester"; ASTM D 3243, "Test for Flash Point of Aviation Fuels by Setaflash Closed Tester".

When aircraft climb rapidly to high altitudes, air dissolved in the fuel is released. Also, rapid evaporation of the volatile fractions of the fuel may cause the fuel to boil. These processes can cause significant quantities of liquid fuel to be carried out of the tank vents along with the released air and fuel vapor. The development of JP-4 was partially a result of the excessive boil off losses experienced with the more volatile JP-3. Boil off losses are a function of the vapor pressure, and are one of the reasons for controlling and measuring this parameter.

Viscosity is a measure of the resistance to flow exhibited by a fluid. Aircraft and engine fuel systems are designed to operate with liquid fuels having a specified range of viscosity so that fuel lines, valves, and pumps can be of minimum size and weight.

Viscosity of jet fuels is strongly temperature dependent, so the viscosity of the fuel at the minimum operating temperature is of primary importance. The effect of viscosity on fuel atomization is also of importance. The evaporation of the fuel and the mixing of the fuel and air to form a combustible mixture are highly influenced by the fuel nozzle performance, which is strongly dependent on the viscosity. Engine manufacturers generally specify a maximum fuel viscosity on 12 centistokes for reliable engine starting. For JP-5, JP-8, Jet A, and Jet A-1 kerosene fuels, this limits starting capability to temperatures above about -20 to -30°C. The kinematic viscosity of a fuel is determined by measuring the time required for a fixed volume of fuel, at a prescribed temperature, to flow through a calibrated capillary tube. The standard viscosity test method is ASTM D 445, "Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosities)".

The freezing point of jet fuel must be below the coldest temperature that can, under any flight circumstance, be reached in the aircraft fuel systems and tanks. If the freeze point is exceeded, the fuel could solidify and stop fuel flow to the engine. Early jet fuel specifications required freeze points of -60°C or below. These extremely low freeze point requirements limited fuel availability, and are now known to have been overly conservative. Probably the most severe environment likely to be encountered by USAF aircraft is at Eielson AFB in Alaska, where ground level temperatures as low as -50°C have occurred for periods as long as 24 hours. Temperatures at altitude can often be lower than -50°C, but aerodynamic heating of the aircraft moderates those temperatures significantly. The freeze point test method, ASTM D 2386, "Test for Freezing Point of Aviation Fuels" is conservative in that the temperature measured is that at which the last crystal of fuel melts. Fuel will still flow at somewhere between 1°C and 10°C below the measured freeze point. Test methods that measure the minimum fuel flow temperature have been suggested as replacements for the freeze point test, but have not yet been adopted.

The combustion performance of jet fuels includes two different aspects, the net heat of combustion, and the burning quality. The net heat of combustion is the lower heating value of the fuel. This assumes that the water formed through combustion remains in the vapor form. Direct methods for determining the net heat of combustion include ASTM D 240, "Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method)". Estimation methods are also used. These include ASTM D 1405, "Methods for Estimation of Net Heat of Combustion of Aviation Fuels (Aniline-Gravity)", and ASTM D 3338, "Method for Estimation of Heat of Combustion of Aviation Fuels". ASTM D 3338 uses a correlation based on the density, distillation temperatures, and the volume percent of aromatics. The minimum net heat of combustion specified for the standard fuels is seldom, if ever, approached. Limits of other fuel properties are generally much more restrictive.

Burning quality requirements are related to excessive exhaust smoke and carbon deposition problems. The specifications for JP-1, JP-2, JP-3, and initially for JP-4, had no requirements regarding the burning quality of the fuel. However, severe problems in these areas were observed in early turbine engines and lead to recognition of the need to characterize and specify burning quality. Fuel combustion performance parameters employed in fuel specifications have included Smoke Point, Smoke Volatility Index (a calculation using Smoke Point and the volume percent of fuel that evaporates below 204°C), and Luminometer Number (essentially an automated Smoke Point method). Combustion research conducted in the 1950's and 60's indicated a close correlation between the combustion performance of a fuel and its hydrogen/carbon ratio (or hydrogen content). U. S. military jet fuel specifications now include a minimum hydrogen content or Smoke Point. Commercial specifications generally rely on the Smoke Point and Luminometer Number methods. ASTM D 1322, "Test for Smoke Point of Aviation Turbine Fuels", involves burning the fuel sample in a wick lamp, and measuring the height of a flame that can be obtained without the formation of soot at the flame tip. This simple test was originally developed for illuminating kerosenes, but has proven to be quite suitable for turbine engine fuels. ASTM D 1740, "Luminometer Numbers of Aviation Turbine Fuels", is no longer used for military turbine fuels, but is still required in commercial fuel specifications. To measure the hydrogen content of a fuel, the preferred test method is ASTM D 3701, "Hydrogen Content of Aviation Turbine Fuels by Low Resolution Nuclear Magnetic Resonance Spectrometry". Methods previously used include ASTM D 1018, "Test for Hydrogen in Petroleum Fractions" (a combustion method), and ASTM D 3343, "Method for Estimation of Hydrogen Content of Aviation Fuels" (based on correlations involving fuel density, distillation temperatures, and volume percent aromatics).

Aircraft and engine fuel systems include many different materials in their fabrication. Corrosion of these materials through action of constituents of the fuel must be avoided. ASTM D 130, "Test Method for Detection of Copper Corrosion From Petroleum Products by the Copper Strip Tarnish Method", is a requirement of U. S. military turbine engine fuel specifications. In this test a polished copper strip is exposed to the fuel under controlled conditions, and subsequently examined for corrosion. Absence of corrosion on the test strip indicates that elemental sulfur and corrosive sulfur compounds are not present, and is indicative that there will be no corrosive problems with any of the fuel system materials, as well as copper.

Jet fuel must be clean and dry. Clean of solid particulates and dry of free water, in order to ensure that the flow of metered fuel to the aircraft engine is not interrupted and that the fuel system functions properly and reliably. Water is the most common and potentially serious fuel contaminant. There are many opportunities for water contamination, beginning at the refinery, during fuel storage, transport, and servicing. In sufficient quantity, water that is pumped to the engine, along with a diminished quantity of fuel, can cause engine flameout. Water can also freeze within the fuel system, blocking fuel flow to the engine. In addition, water promotes the growth of micro-organisms within fuel systems, leading to plugging of filters, and corrosion problems. At 25°C, turbine engine fuel can hold up to 70 parts/million of water in solution. When the fuel is exposed to low temperatures, such as occurs during high altitude flight, much of the dissolved water condenses. With aviation gasoline, any suspended water rapidly separates and settles to the bottom of the tank where it can be drained. Turbine engine fuels, being more dense and viscous than gasoline, tend to hold the water in suspension. If surfactants (surface active agents such as soaps and detergents) are also

present, fuel-water emulsions may form and prevent the usual gravity effect separation of the water and the fuel. Filter-separators are used to remove solid particulates and undissolved water from fuel during ground transfer and fueling of aircraft. Filter-separators consist of a depth filter, a coalescence media, and a hydrophobic membrane, installed within a pressure vessel. The surfactants that can prevent gravitational separation of water from fuel can also interfere with filtration, coalescence and water separation.

Specification test methods used to control water contamination of turbine engine fuels include the Water Tolerance Test, and the Water Separometer Index. The Water Tolerance Test was developed for aviation gasoline, to determine if alcohols or other water soluble agents were present. In this test, 20 ml of distilled water are added to 80 ml of fuel. The mixture is shaken for 2 minutes, and then allowed to settle. Any increase in volume of the water bottoms indicates that some water soluble material was extracted from the fuel. Appearance of bubbles or "lace" at the fuel/water interface indicates the presence of surfactants that may interfere with the separation of water from the fuel. This test method, ASTM D 1094, "Test for Water Reaction of Aviation Fuels", is specified in jet fuel specifications, as it is easily conducted in the field with a minimum of equipment. The Water Separometer Index was developed by Dr. John Krynitski of the Naval Research Laboratory in the late 1950's. He developed a miniature coalescer test device that was found to be quite sensitive to the presence of surfactants in fuel. A variation of the device is used in ASTM D 2550, "Test for Water Separation Characteristics of Aviation Turbine Fuels", which became a turbine engine fuel specification requirement in 1964. In the test, water is added to the test fuel, the fuel/water mixture is emulsified, the emulsion is pumped through a coalescence media, and the degree of fuel/water separation is measured using a transmissometer. In March 1969, the Water Separometer Index, Modified (WSIM) replaced the WSI method. Neither the Water Retention Test nor the WSIM test, however, gives good correlations with actual field performance of filter-separators. The performance of the filter-separators may only gradually degrade over months of service, as thousands of gallons of different batches of fuel are filtered. The Water Reaction Test and the WSIM are run on a single fuel, and the tests last for only a few minutes. Never-the-less, these tests helped to reduce the water contamination problems that plagued the Air Force in the late 1950's and early 1960's. One significant use of the WSIM was to screen the MIL-I-25017 corrosion inhibitors for their effect on coalescence. The corrosion inhibitors that seriously degraded WSIM ratings were removed from the qualified products list. Their removal from turbine engine fuels significantly alleviated the water in fuel contamination problem.

Specifications for JP-1, JP-2, and JP-3, and JP-4 initially, did not include limits on solid particulate contaminants. The first turbine engine fuel storage and handling systems were converted from aviation gasoline use, and were not noted for delivering clean, dry fuel. The use of fuel soluble corrosion inhibitors was begun in 1954 to inhibit the retard the internal corrosion of ferrous tanks and pipelines, which were major sources of particulates (rust). As new fuel systems built, improved materials and designs were used to reduce corrosion and to aid in the removal of contaminants. Improved fuel storage, handling and servicing systems led to revision, in 1965, of the fuel specification MIL-T-5624 to limit the mass of solid particulates in the fuel to no more than .5 to 1.0 milligrams of solids per liter of fuel. The test method used for measuring solid particulates is ASTM D 2276, "Test for Particulate Contamination in Aviation Turbine Fuels". This method involves filtering of a prescribed quantity of test fuel through a pre-weighed membrane filter, and measuring the increase in filter weight caused by the contaminants.

The 1973 revision of specification MIL-T-5624 included a Filtration Time Test as a new fuel quality control requirement. This test measures the time required for fuel, under controlled conditions, to pass through a specified filter. A high filtration time is indicative of a fuel containing materials that may rapidly plug filter-separators and aircraft fuel line filters. This requirement was added to alleviate filterability problems that had occurred intermittently. Fuel that has been transported by barge or tanker is likely to have poor filterability unless care is taken to ensure that the fuel remains dry. A filter plugging precipitate can be formed by reactions involving corrosion inhibitor/lubricity improver additive, and water containing trace metals. The fatty acids in the corrosion inhibitor apparently react with the trace metals to form a gelatinous precipitate. Other problems, related to the growth of microorganisms found in water bottoms, and the presence of copper, which, when chelated by metal deactivator can form materials that deposit on filters at lower temperatures.

During the development of the Pratt & Whitney J-57 engine in the early 1950's, carbon deposit fouling was encountered in the fuel atomizer nozzles. The severity of the problem was found to vary with different batches of fuel. The ability of a fuel to resist formation of these deposits is called thermal oxidative stability. The immediate solution for the J-57 problem was a redesign of the fuel manifold and nozzles to reduce the amount of heat transferred to the fuel. However, the need to control the tendency of fuels to form deposits when exposed to high temperatures was recognized, and studies of the problem were initiated. Analysis of the deposits revealed the presence of high concentrations of metals, sulfur, nitrogen, and oxygen compounds. Metals such as copper, iron, lead, and zinc were shown to accelerate the formation of deposits at high temperatures. Copper, for example, needs to be present at concentrations of only about 10 to 20 parts per billion to degrade a fuel's thermal oxidative stability.

When various static tests were found to be inadequate in characterizing thermal stability, a dynamic (flowing) test device was developed. This device, later designated as the ASTM-CC Fuel Coker, simulated the engine fuel system by flowing the fuel across a heated tube, and then through a heated filter. An increase in pressure drop as the fuel flowed through the filter was indicative of inadequate thermal stability. Subsequently, the amount of deposit formed on the heater tube was found to be a more quantifiable indicator of thermal instability. ASTM D 1660, which was required in turbine engine fuel specifications for many years, standardized the use of the Coker. In 1966, the Coordinating Research Council (CC) initiated the development of an improved thermal oxidative stability test method. This culminated in issuance of ASTM D 3241, "Test for Thermal Oxidative Stability of Aviation Turbine Fuels (JFTOT Procedure)". The Jet Fuel Total Oxidative Tester (JFTOT) is essentially a

miniaturized, automated version of the Fuel Coker, requiring less test time and less test fuel. One major problem with both the Coker and the JFTOT was the lack of a good method for rating the amount of deposits that form on the polished aluminum heater tubes. A visual comparison of the deposit with color standards has been used in the rating procedure. The Alcor Corporation, developer and supplier of the JFTOT, developed a Tube Deposit Rater (TDR) that measures the change in heater tube reflectivity caused by the deposits. For JPTS and JP-7 fuels the JFTOT test method and the Alcor TDR method are specified. To further improve the tube rating procedure, the JFTOT heater tube is rated both before and after the test, and the maximum increase in the TDR rating caused by deposits is the criterion used. This method provides good precision and removes the subjectivity of the visual rating method. One basic problem that occurs with the use of a simulative test device, such as the Coker or the JFTOT, is the need to increase test severity so as to shorten test time. In a turbojet engine, fuels with poor thermal stability may cause debilitating deposits only after hundreds of hours of operation. For quality control testing, the tendency of the fuel to form deposits must be determined using a test that can be run in a few hours. In order to do this, test temperature is increased in order to obtain deposits in a limited time period. This approach is valid only to the extent that only the reaction rates, and not the actual reactions, vary with the temperature. In the development of JP-8+100 the Air Force has developed a number of test rigs to verify this assumption, and to provide a true, long duration evaluation of a test fuel.

The color of a petroleum product can often reveal the presence of contaminants and may even be used to identify the contaminating material. Dyes are used to identify petroleum products. For example, hydraulic fluid is dyed red, Grade 100 low lead aviation gasoline is dyed blue, and Grade 100 aviation gasoline with tetraethyl lead is dyed green. A sample of jet fuel that has a red, blue, or green tint would be suspected of being contaminated with one of these other products. Turbine engine fuels are generally not dyed, and their natural color ranges from water white to straw. Although some military turbine engine fuels initially required that the fuel color be reported, no current specification places limits on color. ASTM D 156, "Saybolt Color of Petroleum Products (Saybolt Chromometer Method)", was the test method normally specified. The Saybolt Color is related to the depth of a column of fuel sample, the color of which is compared with specified standards. The greater the number (between -16 and +30), the lighter the color.

Hydrocarbon fuels slowly oxidize during storage to produce soluble and insoluble gums or resins. Soluble gums will leave deposits upon evaporation. Gums in gasoline, for example, leave deposits in intake manifolds and on intake valves of reciprocating engines. When the first specifications for turbine engine fuels were written, the effects of gums in turbine engines were not known. It was assumed that insoluble gums could affect fuel metering pumps, fuel valves, and fuel filters, so the existent gum requirements for aviation gasoline were carried over into the turbine engine fuel specifications. Tests run about 1950 by the Air Force at Wright-Patterson AFB were used to determine the importance of existent gums in turbine engine fuels. A J-65 engine, which used vaporizer tubes for fuel atomization and injection, was employed for the tests. The vaporizer tubes were candy cane shaped tubes through which a portion of the combustion air and all of the fuel passed before entering the combustor. The vaporizer tubes extended into the combustion chamber where heat from the burning fuel helped to vaporize the entering fuel. The fuel and air then exited the vaporizer tube near the dome of the combustor. Fuel gum was suspected as a factor in the burnout of vaporizer tubes in the J-65 engine. Tests were conducted with fuel that had been doped with roofing tar, used to simulate gum. The tests showed that existent gum levels in excess of 20 milligrams of gum per 100 milliliters of fuel caused premature burnout of the vaporizer tubes. Therefore, a maximum allowable existent gum content of 10 mg/m was selected for turbine engine fuel specifications.

Hydrocarbon fuels are excellent electrical insulators, and electrostatic charging occurs as fuel flows through fuel system components. This electrical charge can accumulate, and produce incendiary spark discharges. Many aircraft fuel system fires have resulted. Static dissipative fuel additives, that increase the electrical conductivity of fuel, have proven effective in suppressing electrostatic spark discharges in conventional aircraft fuel systems. The electrical conductivity of fuel is measured by subjecting the fuel to a known voltage potential, and measuring the resulting current flow. This allows the resistivity of the fuel to be calculated, and conductivity is simply the reciprocal of resistivity. Test methods for conductivity include ASTM D 2624, "Test for Electrical Conductivity of Aviation and Distillate Fuels Containing a Static Dissipator Additive", and ASTM D 4308, "Standard Test for Electrical Conductivity of Liquid Hydrocarbon Fuels by Precision Meter".

E. ADDITIVES

Fuel additives are chemicals that are added to fuels to impart specific properties, or to counter the effects of fuel contaminants that can not easily be removed. Extreme care must be used in selection of turbine engine fuel additives. Additives intended to enhance performance of the fuel in one aspect can have serious deleterious effects on other fuel properties. Additives that contain metallic compounds can attack engine hot section components, such as the combustor and turbine. Solvents and other additives constituents can attack elastomeric materials used in aircraft and engine fuel systems, cause corrosion of close fitting components of fuel pumps and fuel controls, and degrade thermal oxidative stability. A large variety of fuel additives have been developed and investigated over the years, and several are still in use in military turbine engine fuels. The major ongoing turbine engine fuel development program today is the JP-8+100 program, which relies on a special additive package to improve the fuel thermal stability. The following paragraphs contain discussions of the various additive types, including development history, utility, and present status.

Antioxidant additives are added to turbine engine fuels and other petroleum products to prevent the formation of gums and peroxides during storage. Antioxidants function by reducing or preventing the formation of free radicals in the fuel. Reduction of

the free radicals reduces the formation of gums and peroxides. Peroxides normally form in fuels during prolonged storage in the presence of oxygen. They are deleterious to thermal oxidative stability, possibly being precursors to the formation of deposits. Peroxides also attack fuel tank polysulfide sealants and other fuel system elastomers. There have also been reported problems with neoprene and nitrile rubber fuels hoses, sealing rings, and diaphragms, due to the action of peroxides.

The failure of a fuel control diaphragm was found to be the cause of a crash of a U. S. Navy A-7 aircraft in 1976. Peroxides were the suspected cause of the diaphragm failure. Through extensive laboratory testing, the Navy demonstrated the ability of antioxidants to prevent formation of peroxides in turbine engine fuels. As a result of this work, antioxidants were required in all JP-5 fuel.

The two basic types of antioxidants used in turbine engine fuels have been phenyl diamines and hindered phenols. The phenol diamines are no longer used because they have been found to degrade the thermal stability of the fuel. The hindered phenols have no negative effect on thermal stability, and at high concentrations of 5000 parts per million, or more, have shown a slight improvement in thermal stability.

Two test methods usually used to demonstrate the effectiveness of antioxidants are ASTM D 525, "Oxidative Stability of Gasoline (Induction Period Method)", and ASTM D 873, "Oxidative Stability of Aviation Fuels (Potential Residue Method)". In these test methods the candidate antioxidant is added to a fuel, which is then pressurized with oxygen and heated to 100°C. The ASTM D 525 test method measures the induction time required for the oxygen uptake to reach a prescribed rate. The ASTM D 873 test method measures the amount of residue (gum) formed after a fixed period of time. ASTM D 3241, "Thermal Oxidation Stability of Turbine Fuels (JFTOT Procedure)", is also used to insure that an antioxidant does not degrade fuel thermal stability.

Turbine engine fuels that have been subjected to severe hydrogenation processes lose their natural antioxidants, and are subject to rapid peroxidation. Hydrotreated fuels must have antioxidants added before the fuel is exposed to the atmosphere. This is because antioxidants do not reverse oxidation reactions that have already occurred. The use of hydrotreating and hydrocracking processes in the production of turbine engine fuels is increasing, and as a result, the importance and need for antioxidants is also increasing. Normal antioxidant concentrations in turbine engine fuels range up to 14 milligrams per liter.

Metal deactivator additives (MDA's) were initially added to gasolines that had been treated using the copper sweetening process (a method to convert mercaptan sulfur compounds to less noxious sulfur compounds). Copper is known to catalyze oxidation reactions that form gums, so MDA was used to deactivate any traces of copper left in the fuel. MDA's function by forming a chelate with the metal. The chelate effectively isolates the metal from the fuel.

MDA's are optional additives in military turbine engine fuels. They are included at the discretion of the fuel producers. They are likely to be used when contamination of the fuel by trace metals, especially copper, has occurred or is suspected. Although developed primarily for use with copper, the MDA's are also effective with some other metals, such as lead. U. S. Navy studies with jet mix (two parts JP-5 and one part aviation gasoline) showed excessive gum formation unless either an MDA was added, or the tetraethyl lead was removed from the gasoline. MDA's are approved for use in military turbine engine fuels at concentrations up to 6 milligrams per liter.

In 1954 the U. S. Government began using commercial pipelines to transport aircraft fuel to Air Force facilities. To combat the excessive corrosion in the ground fuel systems, and to reduce the carryover of corrosion products into aircraft fuel systems, corrosion inhibitor additive requirements were added to specifications for both aviation gasoline and turbine engine fuels. A specification (MIL-I-25017) was issued in 1954 for corrosion inhibitor additive. It included a 20 hour corrosion test (also known as the rust test) to qualify additive candidates and to determine the minimum effective concentrations (MEC's).

Problems with fuel/water separators were traced to the action of the corrosion inhibitors. Some of the approved additives chemically reacted with undissolved water and trace metals to form a gelatinous material which rapidly plugged the filters. In March 1960 corrosion inhibitors were removed from the specification for turbine engine fuels. In September 1962, they were again made a mandatory requirement, but the specification was revised to require a minimum Water Separation Index rating. This revision of the specification resulted in the removal of several suppliers from the Qualified Products List (QPL).

The mandatory requirement for corrosion inhibitor additive was again removed from the turbine engine fuel specification in November 1965. Within a few weeks, the Air Force began to experience major fuel lubricity problems with fuel pumps and controllers. Field problems were experienced with J57, J69, and J79 engines. When pilots attempted to throttle back the engines during decelerations, response from the fuel controller was either sluggish or non-existent. As a result the engine would be stuck at full throttle. This was due to inadequate lubrication of the spool/sleeve servo system in the fuel controllers. Poor fuel lubricity also caused excessive wear on pump gears and pistons, and decreased the mean time between failures.

Distillate fuels contain sulfur, nitrogen, and oxygen compounds. These impurities are effective boundary lubricants. However, when fuels are hydrotreated, the naturally occurring boundary lubricants are removed or destroyed. The corrosion inhibitor additives prevent corrosion by plating out on metal surfaces to form a protective film. This film, which prevents oxygen from reaching the surface to cause corrosion, also acts as a boundary lubricant. When corrosion inhibitor additive was removed from

fuels in 1965, the fuels no longer exhibited the lubricating properties that the fuel pumps and controllers had been designed to rely upon.

In November 1966 the Air Force again modified the turbine engine fuel specification to require addition of corrosion inhibitor. Problems due to inadequate fuel lubricity disappeared immediately. The few problems reported since then have all been traced to inadequate amounts of additive, and injection of additional additive into the fuel has always resolved any problems.

The only problem remaining, in the area of fuel lubricity, was the fact that the qualification of the additives that affected lubricity, and determination of their minimum effective concentrations, was established by a test that evaluated effectiveness in preventing corrosion, rather than lubricating capability. Various agencies were attempting to develop a suitable test to measure the tribological properties of a fuel, and determine the effectiveness of lubricity additives under different conditions. Test rigs to evaluate lubricating oils operating in the hydrodynamic lubrication mode were available, but fuel pumps and controllers operate in the boundary lubrication regime, so those rigs were not of use.

One of the first fuel lubricity testers was built by Bendix, under the guidelines established by the Coordinating Research Council (CRC), and was known as the Bendix-CRC Lubricity Tester. This device attempted to simulate a typical valve and sleeve unit in a fuel controller. The friction force of the spool sliding in the sleeve was measured. About the same time, in Great Britain, problems were being encountered with high pressure, piston type fuel pumps. A pin-on-cylinder (POC) tester, which consisted of a silver plated bronze pin, rubbing on a steel cylinder, was used to simulate the pump hardware. Fuel lubricity was evaluated by measuring the wear rate of the pin. Another early tester was the Furey Ball-On-Cylinder (FBOC), which was used to study the metallic contact and friction between sliding lubricated surfaces. The dynamic friction force of the ball, in contact with the cylinder, the major and minor axes of the elliptical wear patterns (wear scar) on the ball, and the percent metal contact between the ball and the cylinder were all measured. The FBOC was first used to test fuel lubricity in 1966. It was much more sensitive than the POC for evaluating small amounts of corrosion inhibitor, but it had poor precision. In 1984 the Air Force contracted with the InterAv Corporation to redesign and improve the FBOC. This resulted in the first version of what is now known as the Ball-On Cylinder Lubricity Evaluator (BOCLE). The BOCLE provides a quantitative measure of fuel lubricity in terms of the wear scar diameter on the ball.

In 1985 the Air Force initiated a program to refine and standardize the BOCLE. The CRC also created a task force to standardize the BOCLE apparatus and the operating procedure. As a result, mandatory use of the Falex Ring, SKF Swedish Balls (12.7 mm in diameter) was specified, and Isopar M-130 ppm DCI-4A was selected as the standard calibration fluid. In running the BOCLE test, the fluid to be tested is placed in a reservoir in which atmospheric air is maintained at 10% relative humidity. The non-rotating ball is held in a vertically mounted chuck, and is forced with an applied load, against an axially mounted steel test ring. The test ring is rotated at a fixed speed and receives a momentary exposure to the test fluid at the bottom cycle of each revolution. The wear scar generated on the test ball is viewed under a microscope, and the major and minor axes of the elliptical wear scar are measured.

In June 1989 the Corrosion Inhibitor/Lubricity Improver (CI/LI) specification was revised to include the BOCLE test. In November 1989, the BOCLE test was approved by the ASTM and ASTM D 5001, "Standard Test Method for Measurement of Lubricity of Aviation Turbine Fuels by the Ball-On-Cylinder Lubricity Evaluator (BOCLE)", was issued. Another important change in the specification occurred in June 1989. At that time ASTM D 2550 was replaced by ASTM D 3948, "Method for Determining Water-Separation Characteristics of Aviation Turbine Fuels by Portable Separometer". The specification was changed to require that the Recommended Effective Concentration (REC) be determined by the rust test, as described in the specification; but should be no less than 6 grams per cubic meter, since the rust test has poor precision at concentrations less than that. The MEC is the larger of: (1) 1.5 times the REC as determined by the rust test, or (2) the amount of lubricity improver that shows a wear scar no more than .65 mm when using the BOCLE in the prescribed procedure. The maximum allowable concentration (MAC) is specified as the lowest of (1) 54 grams of inhibitor per cubic meter of fuel, (2) four times the REC as indicated by the rust test, (3) the highest concentration giving a micro separometer reading of 70 (on a scale of 0 to 100) or higher, and (4), the highest concentration giving less than a 40% change in the electrical conductivity with fuel containing static dissipator additive. All turbine engine fuels procured by the U. S. Military now contain CI/L additive that meets these specifications. As a result, the occurrence of lubricity related incidents, water separation, and filtration problems has been nearly eliminated.

Water contamination in aviation fuels has always been a serious problem. In liquid form, water can cause temporary flameout in the engine, but in solid form (ice), it can block filters and fuel lines, and completely stop the flow of fuel to the engine. In the 1940's and 1950's, free, undissolved water in fuel was suspected as the cause of many in-flight incidents and accidents. The crash of a B-52 in 1958 revealed the magnitude of the problem. Sheets of ice were found inside the fuel tanks of the wrecked aircraft. The ice had cut off the flow of fuel to five of the eight engines, causing the B-52 to crash.

A major research and development program was initiated to solve the water-in-fuel problem as a result of the B-52 crash in 1958. One objective was the development of a fuel system icing inhibitor (FSII). The FSII was to be added to the fuel, but would preferentially migrate to any free water present, and act as an antifreeze. The Phillips Petroleum Company developed a proprietary FSII known as Phillips 55MB. This was tested and accepted for use in Air Force fuels, beginning in 1962. The FSII consisted of 87.3% ethylene glycol monomethyl ether (EGME) and 12.7% glycerol. EGME and glycerol can be dissolved in fuel, but they are much more soluble in water. The freezing point of the water/FSII solution was about -50°C.

Specification MIL-I-27686, "Inhibitor, Icing, Fuel System", was issued in 1961, for the Phillips 55MB formulation, and military turbine engine fuel specifications were modified to require .10 to .15 percent of FSII in the fuel delivered to the Air Force. Subsequent field experience indicated that glycerol was not completely dissolving in the fuel, and problems were resulting. The specification was changed in September 1962, and again in August 1963 to reduce the glycerol concentration to 2.6%, and then to .4%. In March of 1970, the specification was changed to completely eliminate the glycerol, leaving only the EGME. Problems with the stability of EGME during storage later led to a specification amendment to allow the use of an antioxidant at concentrations up to 150 parts per million.

The U. S. Navy used EGME in JP-5 until about 1984. The EGME was found to lower the flash point of JP-5 by as much as 3°C, thus reducing the availability, and increasing the cost of the fuel. The Navy developed a new FSII, diethylene glycol monoethyl ether (DIEGME), which is covered by specification MIL-I-85470. DIEGME is slightly less effective than EGME, so a concentration of .15 to .20% of DIEGME is specified. The Air Force adopted DIEGME for use as the FSII in JP-8 in 1993.

One of the benefits of using FSII in turbine engine fuels is that the sumps of aircraft fuel tanks and ground storage tanks can be drained during all weather conditions. Previously, water that collected in the sumps would freeze during the winter and prevent draining until the spring thaw. Another benefit of FSII is that it acts as a biocide to prevent growth of microorganisms in free water. Previous to the use of FSII, fungi and bacteria would grow at the fuel/water interface, using the fuel as a source of carbon. The waste products of the microorganisms were very corrosive, and in the late 1950's caused severe problems in both aircraft and ground fuel storage tanks. The problem was completely eliminated after the introduction of FSII additive. Possible health hazards associated with repeated exposure to DIEGME, however, has led the Air Force to initiate research to replace it with a less toxic material.

Pure hydrocarbons are excellent electrical insulators. When turbine engine fuels and other hydrocarbons flow through pipes and filters, trace contaminants may ionize, resulting in charge separation. (The charges of one sign attach to surfaces, while the charges of the opposite sign remain with the flowing fuel.) This results in a net electrical charge build-up between the fuel and the fuel system components. Fuel system components are electrically bonded to the airframe, and any charges present should safely bleed to ground. However, the charge in the fuel dissipates very slowly, and under certain conditions sufficient charge can accumulate in the fuel and produce incendiary spark discharges. If a fuel/air mixture in the flammable regime is present (such as in the void space of a fuel tank), a fire or explosion can result.

In the 1960's the Air Force experienced one or two static initiated fuel system fires each year. These usually occurred during ground refueling operations. In the late 1960's the fuel tanks of some tactical fighters were equipped with polyester urethane open-pore foam inserts, in order to suppress fires and explosions caused by penetrations of the fuel tanks during combat. The foam proved to be very effective and was responsible for saving many aircraft and their crews during the Vietnam War. In the mid-1970's many of the foam equipped aircraft were returned to the continental United States. Fuel tank fires some began to occur with these aircraft. Although the fuel tank fires were always minor (the foam in the tanks effectively suppressed spread of the fires), these incidents caused great concern. Tests revealed that high electrostatic potentials were generated as fuel flowed through the foam. The use of static dissipator additives (SDA's) in the fuel was proposed as a solution to this problem. A service test of two candidate static dissipator additives, Shell ASA-3 and DuPont Statis 450, was conducted in 1978. These additives can increase the electrical conductivity of fuel by several orders of magnitude, and should allow any charge generated in the fuel to bleed rapidly and safely to ground.

Shell ASA-3 had been used as a SDA in turbine engine fuels since 1962 by other countries in both military and commercial aircraft. It is composed of Aerosol OT (a dispersant) and chromium and calcium salts. In all previous experience with ASA-3 in turbine engine fuels, a minimum fuel conductivity of only 50 picoSiemens per meter was adequate to prevent incendiary spark discharges, and only about .5 parts per million of ASA-3 was normally required. DuPont Statis 450 had not been previously used in turbine engine fuels. However, it contained no metals and appeared to have less of an effect on fuel/water separation characteristics than did ASA-3. Therefore, Statis 450 was included in the service test.

The electrical conductivity of fuel is strongly affected by temperature. A temperature decrease of 20 to 40°C reduces fuel conductivity by about 50%. Laboratory tests indicated that the conductivity of the fuel should be between 100 and 700 pS/m to ensure safety with the foam filled fuel tanks. In the service tests, sufficient amounts of the candidate additives were used to increase the conductivity of the fuel to between 200 and 600 pS/m. The service test and subsequent field experience with JP-4 containing the SDA's was disappointing. The increased fuel conductivity did not eliminate static-initiated fires in aircraft with fuel tanks containing the polyester-urethane foam. The failure of the SDA's was attributed to excellent electrical insulation characteristics of the foam. The SDA does not significantly affect the electrical conductivity of the foam. The problem was exasperated by the introduction of an improved life polyether-urethane foam. This foam was found to generate even more charge than the old polyester-urethane material, and the number of fuel tank fires increased.

Consideration was given to increasing the conductivity of the fuel to much higher levels. However, the accuracy of fuel tank gauging systems in older aircraft are affected by fuels with very high conductivities, and fires had been observed with fuels having conductivities at least as high as 250 pS/m. Considerable effort has been expended by various agencies attempting to find a solution to the static-charging problem in aircraft fuels tanks with fire suppressing foam. The effectiveness of electrically

conductive foam has been demonstrated in service tests. DuPont Statis 450 is the only currently approved static dissipator additive for turbine engine fuels. Typical concentrations of .5 to 2.0 milligrams per liter increase the fuel conductivity to between 200 and 600 pS/m. This is adequate for aircraft that do not have the foam in their fuels tanks, and at these concentrations, has no adverse effect on water/fuel separators or on engine performance.

Dyes may be added to JP-4, JP-5, and JP-8 to aid in the detection of fuel system leaks. Dyed fuel is used in both static engine runups and in flight tests. After the test, the fuel system is inspected for traces of dye, deposited wherever fuel has leaked and evaporated. Red and yellow dyes are suitable, but yellow is preferred because hydraulic fluid is also dyed red. Dyes are procured in accordance with specification MIL-D-81298, "Dye, Liquid, for the Detection of Leaks in Aircraft Fuel Systems".

A black, smoky exhaust can greatly increase the visibility of an aircraft and have an adverse effect on its vulnerability during combat situations. In the late 1960's the U. S. Navy modified combat aircraft to provide for injection of a smoke suppressant additive into the fuel during combat operations. The additive used was CI-2 (methylcyclopentadienyl manganese tricarbonyl), manufactured by the Ethyl Corporation. Although it was effective in reducing the opacity of the engine exhaust plume, the use of CI-2 was discontinued because of its toxicity and damage that it caused to engine hot section components.

Public concern and laws passed to regulate and limit air pollution have caused consideration of smoke suppressant additives in the fuel for turbojet engine test stands. (Test stands are classified as "stationary sources", and must meet more stringent emission requirements than do aircraft.) Some commercial airlines use CI-2 or Apollo DGT-2 (barium and manganese) additives for the fuel for their test stand operations. Arapahoe Ferrocene (dicyclopentadienyl iron) was selected by the Navy, and later adopted by the Air Force, for suppression of smoke in certain test stands. Ferrocene was selected because it and its combustion products are non-toxic, it causes no long term damage to engines, and it is cost effective. Although the combustion of ferrocene produces iron oxide products that deposit within the engine hot section, the deposits are soft, and blow out of the engine during subsequent engine operation. Some engines suffer temporary performance degradation after a few minutes of operation with ferrocene additivized fuel, because of the iron oxide deposits. Therefore, the use of ferrocene is restricted to short periods of time. The use of ferrocene as a smoke suppressant additive for flight operations was never seriously considered, as the ferrocene degrades the thermal stability of the fuel, causing deposits after long term use.

Halogenated hydrocarbons, generally referred to as halons, are widely used as fire extinguishing and cleaning agents. Although halons are not normally used as additives in turbine engine fuels, there are situations where they may be present. The fuel tanks of some aircraft are protected with halon fire and explosion suppression systems that quickly flood the tank ullage space with Halon 1301 (bromotri-fluoromethane) when a fire or explosion detector is activated. After such an incident, part of the Halon 1301 can dissolve into the fuel and be carried throughout the aircraft and engine fuel system. Prior to the incorporation of Halon 1301 fire and explosion systems in F-16 aircraft fuel tanks, extensive testing was performed to insure that the Halon 1301 would cause no performance or life problems with the F-16 aircraft or its F100 engine.

Very high molecular weight polymer additives are used in pipelines to increase the throughput of crude oils and other petroleum products. The additives are added to the products at concentrations of 10 to 100 parts per million. They work by suppressing turbulence, causing the fluid to flow in the plug flow mode, and thereby reducing friction. Pipeline friction reducing additives (also known as pipeline drag reducing additives) have been considered for use in turbine engine fuels to increase the flow capacity of turbine engine fuel pipelines.

Similar additives have also been tested as antimisting agents to reduce the formation of flammable mists in the event of an aircraft crash. Concentrations as high as .3 percent are needed to obtain adequate antimisting performance.

Both pipeline friction reducing additives and antimisting additives degrade under high shear stresses, as the long molecular chains of the polymers are broken or cut. Special additive injection systems are required to prevent high shear conditions, and additive reinjection may be needed after the fuel has passed through a high speed pump or other high shear device. There has been general resistance to the use of these additives because of filtering difficulties caused by the presence of very high molecular weight polymers. Also, the polymers cause high existent gum readings. Combustion tests of fuels with the additives indicate little effect. This is probably because the shear forces encountered by the fuel while being pumped to the combustor significantly degrade the high molecular weight polymers.

Prior to initiation of the JP-8+100 program, DuPont Jet Fuel Additive Number 5 (JFA-5) was the only turbine engine fuel additive used for improvement of thermal oxidative stability. This proprietary additive has been required in JP-TS since March, 1970. JFA-5 is an ashless mixture of polymers, organic amines, and amides, in a kerosene carrier. The concentration of JFA-5 used in JP-TS is 3 to 4 pounds per 1000 barrels of fuel (about 9 to 12 milligrams /liter). The effectiveness of JFA-5 in improving the thermal stability of jet fuels was well documented in small scale test devices. Fuel coker tests indicated that tube deposits and filter pressure differentials were significantly reduced when the JFA-5 was added to the test fuel. The effectiveness of JFA-5 was believed to be at least partially due to its dispersive qualities, which prevent fuel degradation products from agglomerating into particles large enough to plug filters or deposit onto surfaces. One problem that results from the dispersive effects of JFA-5 is a reduction in the effectiveness of fuel/water separation.

The JP-8+100 research program was initiated by the Air Force, in cooperation with other government agencies, industry, and universities, in 1989. The main goal of the program was to increase the heat sink capability of JP-8 fuel by 50 percent, by increasing the fuel operating temperature by 100°F, from 325°F to 425°F. This was to be accomplished by developing additives to blend with the fuel at a cost of one dollar or less per 1000 gallons of fuel. It was felt that fuel development was the best compromise to balance the engine performance requirements (technology needs), fuel cost (economic factors), and fuel availability (strategic factors). JP-8+100 will alleviate the need for development of expensive specialty fuels such as JP-7 and JP-TS for future advanced aircraft, and will decrease maintenance costs for current inventory aircraft.

To meet the JP-8+100 goal, five major research tasks were identified. These were:

1. Identify and develop new test techniques for evaluating fuel thermal stability.
2. Advance fundamental understanding of fuel thermal stability.
3. Develop global chemistry models and a thermal stability scale.
4. Formulate effective additive packages for improving thermal stability.
5. Demonstrate, through actual aircraft operation, the performance and cost savings provided through the use of JP-8+100.

In testing a fuel to evaluate its thermal stability performance for actual aircraft use, there are several major hurdles that must be overcome. These include: the complex thermal history, dependent on both mission and aircraft, to which the fuel is exposed prior to combustion; the variation in fuels, which is dependent on the source of the petroleum basestock; and, the numerous mechanisms for deposit formation. The foremost problem is that any laboratory testing must be accelerated by increasing the temperature or oxygen availability in order to obtain measurable deposits in time scales and with fuel quantities appropriate to laboratory testing. Increasing the temperature increases the rate of deposit formation, but is valid only to the extent that the deposit forming reactions are the same ones that would occur at the lower temperatures that the fuel would experience in actual service use. Increasing the oxygen availability can, again, increase the rate at which deposits form, but the validity of such deposits is suspect.

The approach used in the JP-8+100 program has been to develop and employ a variety of static and flowing tests, the results of which, when viewed in the aggregate, and coupled with an enhanced understanding of the nature of deposit formation, can be used to assess the relative thermal stability of a fuel with a specific additive package. Using this general approach, a large number of additive packages, supplied by the additive manufacturers, were screened to establish their effectiveness. Those found most effective were subjected to additional testing and concentration optimization. To quantify additive effectiveness, a linear scale based on the performance of JP-TS was devised. Through this process, additive package candidates were narrowed down to a few that could be evaluated in extended duration tests and simulations. As a result, several additive packages that can meet the JP-8+100 goal were identified. Testing currently underway is establishing material compatibility guidelines, and addressing other operational issues. Flight tests are demonstrating the maintenance cost savings available through the use of JP-8+100 in current inventory aircraft and engines.

F. MISSILE FUELS

The requirements placed on fuels for ramjet and turbine engine powered missiles vary greatly from those placed on fuels for conventional aircraft. A missile is generally used for a single mission of relatively short duration. The range of a missile is limited by the amount of fuel that can be carried on board. The volume of the fuel is often more important than the weight of the fuel. Since only a small amount of fuel will be used for the life of the missile, the cost of that fuel becomes nearly insignificant in comparison with the overall cost of the missile. Storage stability of the fuel can be a critical parameter for missiles, while thermal oxidative stability is generally much less important than it is for aircraft engines that may accumulate thousands of hours of use. Low temperature and low pressure performance may be important considerations for missiles with high altitude missions.

Prior to the development of the Navy's Talos missile in the early 1960's, the only fuels available for turbine engine powered missiles were JP-4 and JP-5. Historically, the search for improved range fuels began in the 1950's when the National Advisory Committee for Aeronautics (NACA) began investigating available hydrocarbons having heating values greater than those of the conventional aircraft fuels. It was 1965, however, before the Bendix Aerospace Systems Division, developer of the Navy's Talos surface to air missile, began actively investigating the use of high density, high energy fuels to extend the range of the missile. One of the candidate fuels was a commercial byproduct, methylcyclopentadiene dimer (MCPD), which had excellent energy/density properties. However, when tested, MCPD was found to be chemically unstable, having a tendency to form precipitates and viscous gums, even under a nitrogen blanket. After consultation with personnel of ESSO Laboratories and the Applied Physics Laboratory (APL) of Johns Hopkins University in June 1966, a decision was made to hydrogenate MCPD, with the hope of producing a more chemically stable fuel. Testing of the resulting fuel, tetrahydromethylcyclopentadiene dimer (T-H Dimer), revealed that it did have acceptable storage and materials compatibility properties. As a result, in early 1967 the Navy issued a specification for T-H Dimer. The Navy specification was superseded later in 1967 by a tri-service specification, MIL-F-82522, and the fuel was designated RJ-4. RJ-4, which has a volumetric heating value approximately 16% greater than that of JP-5, was, in 1968, selected to replace JP-5 in the Talos missile. It was later selected for the Navy's Tomahawk missile, as well.

A fuel, norbornadiene, with a volumetric heat value even higher (by 15%) than RJ-4 was initially investigated by the Air Force Aero Propulsion Laboratory as early as 1962. Using norbornadiene as the feedstock, the Shell Oil Company developed and, in 1966, patented a new fuel, known as Shelldyne-H. (Shelldyne-H was later designate RJ-5.) In 1970, the Air Force sponsored additional work at Shell for production of 1664 gallons of Shelldyne-H by the batch method, and for development of process techniques and quality control procedures. In 1972 an additional contract was awarded to Shell for production of 5000 gallons, and the development and demonstration of a distillation process with a capacity of 200 gallons per day. In 1974, contracts were awarded to the Sun Oil Company and the Ashland Oil Company to improve the production process, and procure additional RJ-5 fuel.

RJ-5 was designated for the Air Force's Advanced Strategic Air Launched Missile (ASALM). Flight tests of the integral rocket/ramjet powered ASALM in 1979 and 1980 were very successful, but the program was not carried into production. During development testing of the ASALM engine, RJ-5 was found to have a freeze point problem. Originally, it was thought that RJ-5 had a freeze point below -65°F. However, on one occasion it was found to be frozen at a higher temperature. Careful evaluation showed that RJ-5 can readily be supercooled to well below its true freeze point of about -30°F. Much of the ASALM technology was transitioned into the Navy's Supersonic Low Altitude Target (SLAT) program, but no further development of RJ-5 continued because of the freeze point problem.

In January, 1973 the Air Force funded its first program to develop a liquid hydrocarbon fuel, superior to RJ-5, for use in missiles. The Sun Oil Company was contracted for high density hydrocarbon fuel formulation and development. Under the direction of Dr. Abe Schneider, Sun's Scientific Advisor, the formulation for JP-9 was established, and a feasible process to produce JP-10 was developed.

The Air Launched Cruise Missile (ALCM) evolved from the Subsonic Cruise Armed Decoy (SCAD) and Subsonic Cruise Unarmed Decoy (SCUD) programs. Dr. Herb Lander of the Air Force Aero Propulsion Laboratory convinced the program office that JP-9, with properties similar to JP-4, but with higher energy, should be considered as the fuel for the SCUD/SCAD missiles. At that time, JP-9 was formulated as a blend of RJ-4, RJ-5, and methylcyclohexane (MCH). After cancellation of the B-1 program in 1977, development of the ALCM became a high priority. When the SCAD program evolved into the ALCM, JP-9 was selected as the operational fuel.

The fuel, cyclopentadiene, that was to become JP-10, was developed prior to JP-9. ESSO Research and Engineering Company was issued a patent for cyclopentadiene in 1968. This chemical compound has outstanding storage stability, high volumetric heating value, low viscosity, high flash point, and extremely low freeze point. After selection of JP-9 for the ALCM, the advantages of JP-10 began to be recognized, and the RJ-4 component of JP-9 was replaced by JP-10. Ultimately JP-10 itself became the ALCM fuel. JP-9 worked well in the ALCM, but JP-10 was much less expensive and, with a flash point well over 100°F, it was a much safer fuel for ground operations. However, since the ALCM engine had been designed to ignite with JP-9 fuel (with a flash point of 60-80°F), switching to JP-10 severely reduced the ignition envelope. The solution was the use of a priming fluid, PF-1, which consists of about 90% JP-10 and 10% MCH. About a half pint of PF-1 is used for ignition of the ALCM engine. JP-10 has achieved wide acceptance as the fuel of choice for many turbine engine and ramjet powered missile systems. RJ-6, which was a blend of RJ-5 and JP-10, was developed in the late 1970's as a cure for the freeze point problem that had been encountered with RJ-5. Because of the high cost of RJ-6, and the necessity to rely on a foreign source for the norbornadiene feedstock, a reformulation program was undertaken in the 1980's. Since the chemical composition and physical properties of the reformulation differed from the original RJ-6, the reformulation was designated RJ-7. Neither RJ-6 or RJ-7 were attractive enough to warrant replacement of JP-10.

The potential for extending the range of missiles beyond what is possible with conventional high density missile fuels prompted interest in slurry fuels that contain additives, such as boron, carbon, or aluminum in suspension in a gelled form. Such slurry fuels can provide a very high heating value per unit volume. Work by the NACA on boron slurry fuels was begun as early as 1958. In the early 1980's, the Defense Advanced Research Projects Agency (DARPA) funded a program with Vought to develop technology for a high temperature turbine engine to power a long range cruise missile. It was believed that a boron slurry fuel would have high payoff for such a vehicle. In addition, boron slurries were considered for a variety of ramjet engine projects, but none have evolved into operational systems.

Carbon slurries offer a significant increase in volumetric energy content, while creating a minimum of additional problems for system design. In 1978 the Fuels Branch of the Aero Propulsion Laboratory began a major initiative to develop a stabilized carbon slurry fuel, and to take the first steps in defining its combustion requirements. A formulation designated as SF-1 (Slurry Fuel-1) resulted from this effort. In 1981, a second carbon slurry formulation, designated SF-2, was developed. Work on characterization of these fuels for use in turbine engine powered missiles continued through the 1980's, but none of the proposed missiles reached operational status. A small program in the mid-1980's, to evaluate the combustion characteristics of an aluminum slurry fuel, was not successful. A follow-on program, with Sun Oil Company, to study aluminum slurry formulations was the last slurry fuel program funded by the Air Force. The result of the many years of slurry fuel work demonstrated that formulation of stabilized slurry fuels is possible but, to make such fuels a viable option for turbine engine powered cruise missiles, a substantial amount of fuel system and propulsion engineering would be required.

A wide variety of fuel formulations have been used over the years for rocket powered missiles and space-craft. A discussion of these fuels is not appropriate here, as the focus of this paper is on fuels for air-breathing applications. Two fuel types, however, generally associated with rocket propulsion systems, have been considered extensively for air-breathing engines. The first is hydrogen. Hydrogen was actually the first fuel used by von Ohain to power his first turbojet experiments. Hydrogen has long been the fuel of choice for supersonic combustion ramjets, even though considerable effort has been expended in developing designs that could use hydrocarbon fuels for the low end of the supersonic combustion ramjet speed range. The speed at which reactions must take place in the high speed combustion stream of a supersonic combustion ramjet precludes the use of hydrocarbon fuels at the higher end of the speed range. Hydrogen, however, has the problem of being very poor in volumetric energy content, despite being the very best fuel in energy per unit weight. To overcome this deficiency, hydrogen is usually used in its cryogenic liquid form, and its use as a semi-solid slush has even been considered. The problems associated with cryogenic hydrogen have contributed to the lack of success in fielding an operational system employing a supersonic combustion ramjet for propulsion.

A second class of fuels, traditionally associated with rockets, is solid fuels. For rocket engines using solid fuels, an oxidizer must be provided, either separately, or as a part of the fuel formulation itself. For a solid fueled ramjet engine, the oxidizer is provided by the air passing through the engine. Thus, much greater range is available with a solid fueled ramjet engine, than with an equivalent solid fueled rocket engine. Successful flight tests with solid fueled ramjets have demonstrated the readiness of this technology.

H. THE FUTURE

The history of aviation fuel development has gone hand-in-hand with the development and expansion of air vehicle utility. From the early days until the present, fuel has been the enabler, allowing more powerful engines to be conceived, designed, and fabricated. Often, the forward thinking of fuel developers has provided fuel advances long before the engine designers have recognized a need. At other times, the fuel developers have had to push to correct fuel problems that have been the cause of operational problems. The fuel developer of today must have insight into the demands of the future, but must also be careful not to overrun the parts of that vision that can not be fully conveyed to those that hold the fuel development funding purse strings.

The current development of JP-8+100 will, when fully implemented, revolutionize the world of aircraft and engine fuel system maintenance. JP-8+100 will also broaden the temperature limitations currently imposed on fuel system components. If history is an accurate guide, the 100°F increment provided by JP-8+100 will not satisfy for long the demands of the engine designers.

Future aircraft, already being contemplated by the designers, are sure to go faster, fly higher, and place even more demands on the fuel. Fuel's role as a coolant is becoming increasingly dominant as speeds increase, electronic systems expand, and the importance of stealth becomes more prevalent.

The Air Force already has an ongoing program with the goal of developing a fuel that will enable fuel system operating temperatures of 900°F. This fuel, designated JP-900, will completely eliminate the need to recirculate fuel for cooling purposes. There are two radically different approaches to development of this fuel. The first is a totally new fuel produced from hydrocarbons (primarily saturated cyclic paraffins) that have high thermal stability. A second approach, which is more cost-effective, but also more ambitious, is to build on the experience gained in the JP-8+100 program and develop an additive package to extend the thermal stability of JP-8 to produce JP-900.

Current limitations to thermal stability can be attributed, almost entirely, to the presence of dissolved oxygen in the fuel. Elimination of the dissolved oxygen has long been proposed as a solution to the thermal oxidative stability problem. There are a variety of mechanical means for eliminating oxygen from fuels. These methods include: displacement by inert gases; vacuum degassing; the use of semi-permeable membranes through which the fuel, but not the oxygen molecules could flow; and even the use of ultrasonic pressure waves. Real systems, which exhibit partial oxygen depletion, may, however, show an increase in deposition with decreased initial oxygen. It has been shown that an effective degasser would need to achieve an initial oxygen level in the range of 0 to 5 parts per million. A more promising approach to elimination of oxygen dissolved in fuel is to use an additive that acts as an oxygen scavenger.

Triphenylphosphine (TPP) has been proposed as an oxygen scavenging additive. TPP is soluble in fuel, and is believed to react with dissolved oxygen, rather than with peroxy radicals. This pathway to oxygen consumption suggests that it would work at all temperatures, including those encountered during storage, and at temperatures lower than the normal oxidative temperature regime.

NAC-AEGL vs JP-8

MEETING #13

11-12 Mar 99

New Orleans, LA

KEY PLAYERS

Chemical Managers

John Hinz, Glenn Leach, Capt. Kenneth Still

Draft TSD Author

Sylvia Talmage

Reviewers

William Bress, William Pepelko, Robert Snyder

Contributors

IERA / BAFB, HEST / W-PAFB

AGENDA

- Overview
 - John Hinz
- Literature Review & Key Studies
 - Sylvia Talmage
- Current Knowledge/New Research
 - Maj Les Smith & Maj Don Christensen, MD
- Open Discussion
 - HEST/W-P AFB
 - Committee

ORIGINS

- ATSDR Tox Profiles
 - “4 & 7”, “5 & 8” - - drove initial approach
- Amend approach - - focus on 8!!!
 - 8, “universal fuel”
 - 4 & 7 out; 5 for USN use
 - other fuels - support data only
- Review 8’s limited data base - - draw from
 - tox & exposure data, work place, emergencies
 - military experience
 - context & titration

JET FUELS

<u>Fuel</u>	<u>Type</u>	<u>Use</u>	<u>Fate</u>
avgas	light naphtha	piston engines	limited
JP-1/3	gas-kero	early jet aircraft	retired
JP-4	gas-kero	jet aircraft	retiring
JP-5	kerosene	USN aircraft	current
JP-6	special blend	XB-70 (heat stable)	none
JP-7	special blend	*SR-71 (retired)	limited
JP-TS	special blend	*U2 (heat stable)	limited

JET FUELS

<u>Fuel</u>	<u>Type</u>	<u>Use</u>	<u>Fate</u>
JP-8	kerosene	jet aircraft, trucks tanks, heaters, etc.	current
JP-8 + (xxx)	kerosene	additives - heat stable	future
JP-900	JP-8 + add.	Jet aircraft	future
Jet-A	kerosene	commercial aircraft	current
Jet A-1	kerosene	commercial overseas	current
JP-9	special blend	(too expensive)	none
JP-10	c-pentadiene	cruise missile	current
RP-1	kerosene	rocket fuel	current

CHARACTERISTICS

- Fuel constituents defined by
 - A performance specification, not a recipe
 - Distillation (°C)

	1%	65-70%	95%
• JP-4	34	200	254
• JP-8	144	237	272
• JP-5	(constituent of 8)		
- Properties vary by both source and batch
 - Properties tailored/blended to need
 - Significant batch to batch variability
 - source, refining, composition

CHARACTERISTICS



	mean	range
• Aromatic content (%)		
– JP-4	12	4-20
– JP-5	19	9-25
– JP-8	18	9-25
• Flash point (°C)		
– JP-4	-18	---
– JP-5	63	60-72
– JP-8	49	38-66
• Carbon no.		
– JP-4	7	5-12
– JP-8	11	9-16

ISSUES

- Committee's 1st complex mixture
 - Assess as a compound
- Military vs civilian
 - Repeated vs occasional exposures
 - Exposure vs response
- Assessment complicated by
 - Variability of composition
 - 8's limited data base -- acute data poor, more data needed
 - Exposure to vapor vs aerosol -- or both?
 - Vapor standard only?

JP-8: Current inventory - military and civilian



- JP-8 (and Jet-A)
 - Volume and potential for exposure
 - Other fuels less important
 - JP-8 focus of on-going study and our attention
 - Relevance to current inventories, exposures and accidents
 - Capture new Air Force data
- Limit assessment to JP-8
 - Predicate it on 8's data - derive few values
 - Other fuels as supporting data
- Revisit when new AF data available.



USAF Jet Fuel (JP-8) Program

The Institute of Environment, Safety and Occupational Health (ESOH) Risk Analysis (IERA)

Major Les Smith, MS IH
Major Don Christensen, DO, MPH
Brooks AFB, Texas



Overview

- **Jet Fuel Comparison (JP-8 vs JP-4)**
- **JP-8 Jet Fuel Facts**
- **USAF Jet Fuel Program Drivers**
- **Jet Fuel Exposure IH Survey Data**
- **Current Acute Exposure Study**
- **Future JP-8 Study Plans**



Jet Fuel Comparison

- **JP-8 selected as replacement fuel for JP-4 due to extreme fire hazard**
 - 28 Aircraft lost from JP-4 fires in 1970's
 - JP-4 flash point (-28F to 0F)
 - JP-8 flash point (100F to 140F)
- **DoD/NATO single battlefield fuel**
- **Conversion initiated 1974, completed 1996**
- **JP-8 primary composition range C9 to C16**
- **Benzene content of JP-8 approximately 0.005%**
 - Benzene is not added to the fuel, but considered contaminant from crude oil



JP-8 Jet Fuel Facts

- **Magnitude**
 - DoD: 4.5 Billion Gallons/Yr (Vehicles, Equip, Aircraft)
 - » Recognized as Largest DoD Chemical Usage
 - Worldwide (non-DoD): 55 Billion Gallons/Yr
- **Environmental Concerns**
 - JP-8: Heavy, High Flash Point, Dumping Impact
- **Health Issues**
 - Data Gaps in Toxicology (Animal & Human)
 - No Epidemiology Studies Defining Health Effects
 - IH Data Indicates Significant Exposure



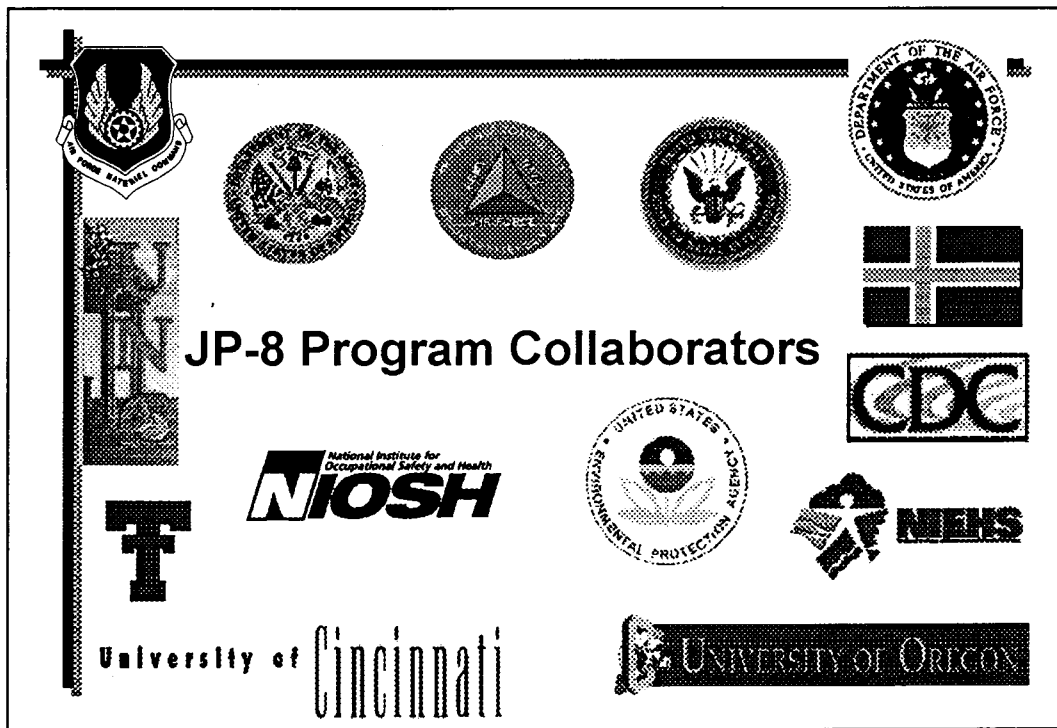
JP-8 Jet Fuel Program Drivers

- Health Concerns
 - Objective Clinical Findings
 - » dermal invasion
 - Anecdotal Complaints
 - » objectionable odor
 - » tasting and belching fuel
 - » dizziness/vertigo
 - » does not evaporate
 - sticks to the skin
 - makes surfaces slippery
- USAF/SG Initiates ESOH Program (Oct 96)



ESOH Jet Fuel Program Milestones

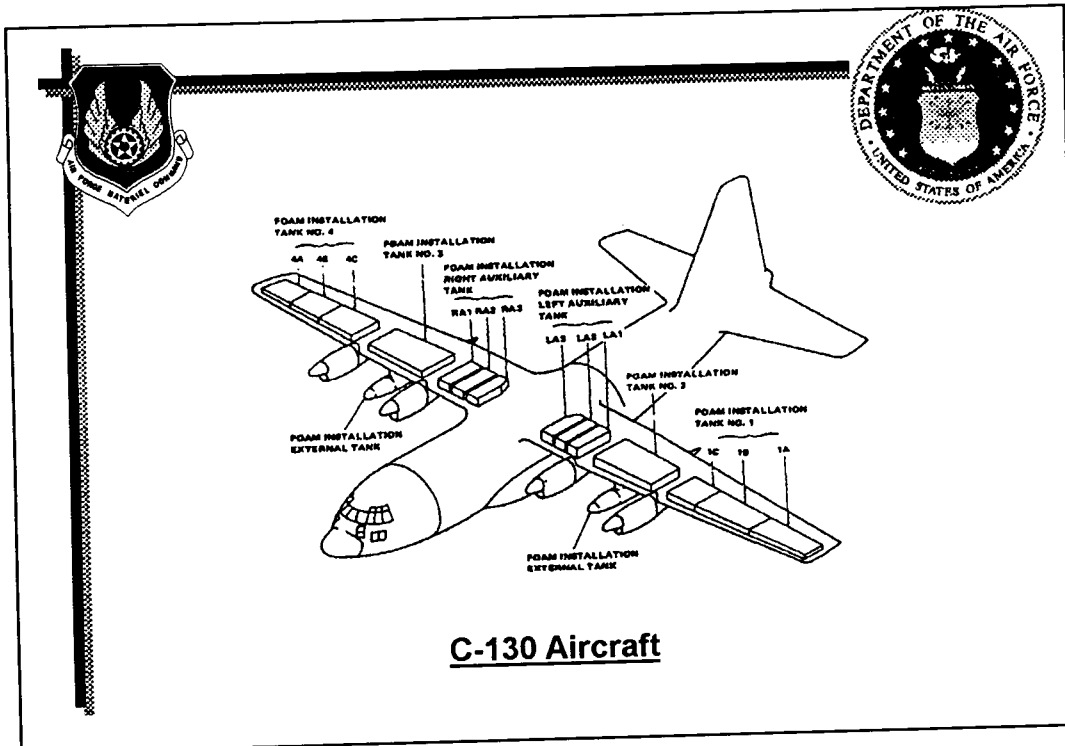
<u>EVENT</u>	<u>DATE</u>
ESOH Jet Fuel Program initiated	Oct 96
US-Norway Jet Fuel Collaboration Agreement	Nov 96
JP-8 Integrated Process Team (IPT) chartered	Mar 97
Benzene Exposure Study (Aircraft tank entry)	Jun 97
JP-8 5-year Study Plan	Nov 97
Neuro Sub-IPT formed	Jan 98
NIEHS Collaboration formalized	Jan 98
International Jet Fuel Conference	Apr 98
Benzene Study (follow-on)	Jun 98
Neuro Test Battery Selection Conference	Aug 98
Texas Tech U. Collaboration (SERDP)	Sep 98
Acute JP-8 Exposure Study Plan initiated	Jan 99



A graphic titled "Extensive IH Survey Details" featuring a central text label and a bulleted list of survey details. The graphic includes logos for the Air Force Department of the United States of America and the University of Cincinnati on the left, and the Air Force Department of the United States of America on the right.

Extensive IH Survey Details

- More than 1000 personal air samples collected
- Personal time weighted averages, STELs, and ambient measurements
- Comparison of three types of workers:
 - Entrant: enters tank, removes foam
 - Attendant: communicates with entrant, passes foam
 - Equipment monitor: runs tools and foam, monitors safety equipment
- Variety of operational aircraft

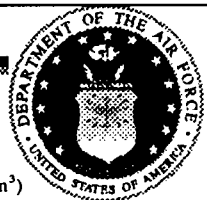


Grab Sampling Benzene in Aircraft Fuel Tank

Grab Sampling Results (GC/MS)

C-130 Left Auxiliary Tank Location		Concentration (mg/m ³)	
<u>Process</u>	<u>Benzene</u>	<u>JP-8*</u>	
Opening hatch before purge	25.56	13,000	
Center cell after purge	1.41	5,200	
Outboard cell after purge	4.15	10,000	
Outboard cell 90-min into work	49.14	-N/A-	

*Entry-safe level JP-8: 4,800 mg/m³ (10% of JP-8 LEL)
 OEL: Benzene = 1.6 mg/m³ and JP-8 = 350 mg/m³



Aircraft Fuel Tank Entry Operations IH Sample Results

Worker Exposures to Benzene and JP-8 Jet Fuel (8-hr TWA, mg/m³)

Chemical	Aircraft Type	Range	Mean	95% Confidence Limits	OEL
Benzene	All	0.002 - 3.30	0.156	(0.113, 0.255)	1.6
	Foam*	0.005 - 3.30	0.203	(0.145, 0.341)	
	No Foam	0.002 - 0.41	0.046	(0.030, 0.103)	
JP-8	All	0.12 - 2308.2	183.08	(112.66, 566.13)	350
	Foam*	0.93 - 2308.2	210.42	(129.66, 526.04)	
	No Foam	0.12 - 79.36	14.17	(7.34, 68.66)	

*Fire Suppressant Foam in Tanks

Worker Exposures to Benzene and JP-8 Jet Fuel (15-min TWA, mg/m³)

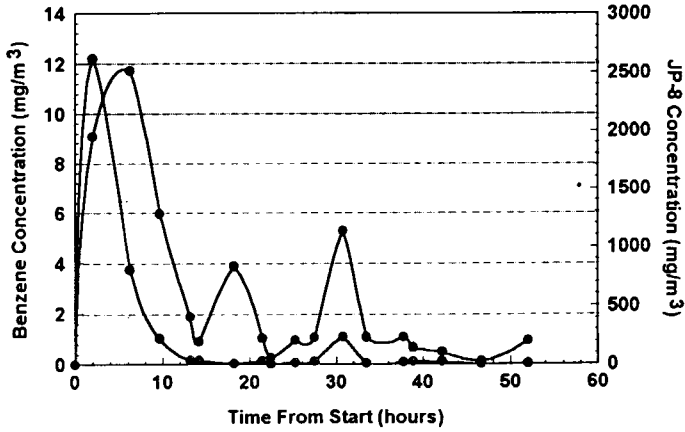
Chemical	Aircraft Type	Range	Mean	95% Confidence Limits	OEL
Benzene	All	0.06 - 41.63	0.644	(0.565, 0.756)	8.0
	Foam*	0.06 - 41.63	0.833	(0.692, 1.058)	
	No Foam	0.08 - 10.83	0.355	(0.318, 0.404)	
JP-8	All	3.85 - 10295.4	266.77	(212.29, 372.74)	1800
	Foam*	6.8 - 10295.4	677.97	(481.90, 1193.14)	
	No Foam	3.85 - 954.23	52.14	(40.877, 72.99)	

*Fire Suppressant Foam in Tanks



Process Task Analysis Timeline Benzene and JP-8

IH Personal Samples for Fuel Cell Repair Operation





Breath Sampling

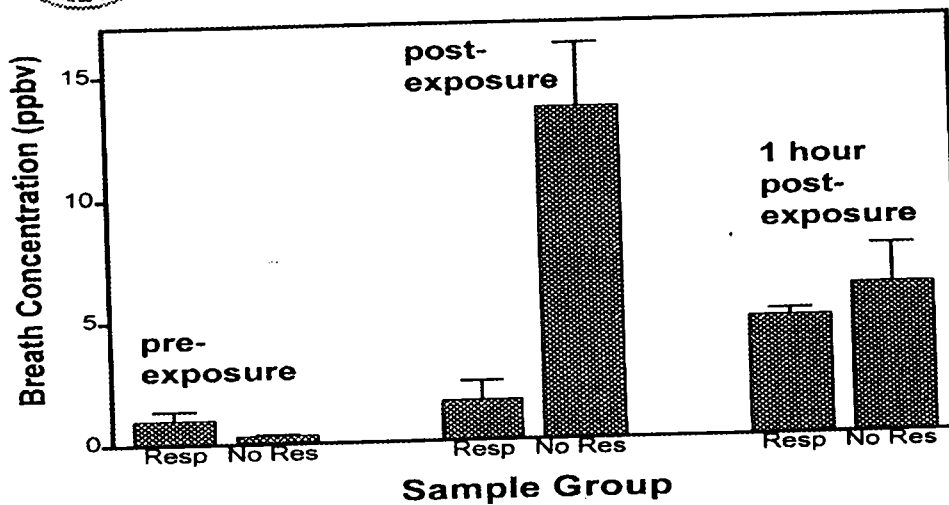
- Collaboration with EPA National Exposure Research Laboratory
 - Mr Joachim Pleil, Methods Development Lab
- Single breath canister (SBC) grab sample method
 - employs evacuated one-liter stainless steel (SUMMA) canisters
 - teflon Mouthpiece
- Simple and self-administered
- Analyze for benzene and JP-8 volatile marker compounds by GC/MS
 - typical JP-8 vapor range of C9 to C12 n-alkanes
 - Selected JP-8 markers: nonane, decane, undecane, and dodecane
- Values ranged from slight elevations to over 100 times the values of an unexposed cohort



Edwards.pzm: Benzene - Tue Nov 24 08:56:39 1998

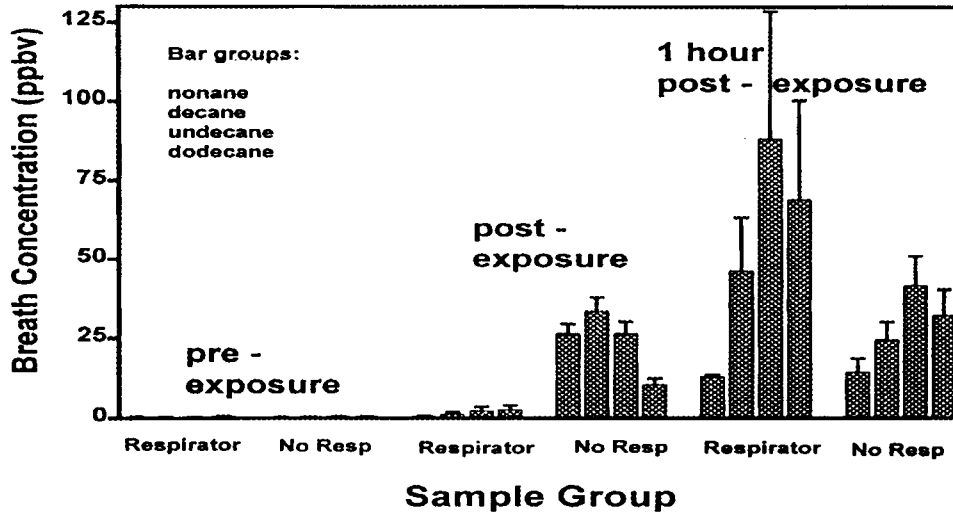


Foam Removal from F-16 Benzene Exposure





Foam Removal from F-16 JP-8 Alkanes Exposure

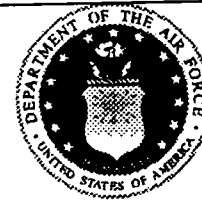


Breath Sampling Results

Aircraft Fuel Tank Workers



- Population means t-test (before/after breath analyses) of workers show that 95% significance that there is exposure to m,p,o,-xylene and C8 - C12 n-alkanes
- Attendants have greater proportional increase for toluene, styrene, C6 to C10 n-alkanes than tank entry personnel
- Tank entry personnel have greater proportional increase for C11 and C12 n-alkanes



General Breath Results

Ubiquitous exposure

- All tested Air Force personnel demonstrate a measurable elevated breath level of C9 to C12 n-alkanes as compared to a group of non-Air Force subjects.
- Alkane levels within USAF group:
 - » Individuals without direct fuels exposures have about 2 to 3 times the alkanes levels of non-AF subjects;
 - » Individuals with direct occupational fuels exposure, but not within the past 4 hours or longer, exhibit up to 100 times the alkanes level of non-AF subjects.



NEXT STEP: JP-8 Breath-Blood Correlation

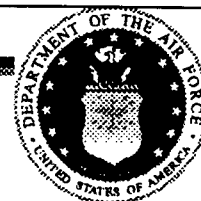
JP-8 Acute Exposure Study (1999-2000)

- During beta test:
 - kinetics of JP-8 in breath
 - conduct long term sampling to measure 2nd, 3rd, ~4th compartments
 - determine correlation of JP-8 levels measured in breath to blood
- Breath Sampling Conducted on all subjects
- Blood Sampling for JP-8 conducted on some subjects (random selection)



Conclusions IH Surveys

- Ambient exposure levels are higher than they should be
 - personnel are adequately protected from inhalation exposure
 - potential exposure through skin absorption
- Highest levels found during tank entry and foam removal
- Levels of JP-8 exceeding 20% of the LEL were recorded during foam repair in the C-130 auxiliary fuel tank
- catalytic sensor LEL meters under report heavy vapor (C9 to C12)



Conclusions IH Surveys

Protective Equipment

- Recommended materials: NITRILE or neoprene provide best breakthrough barrier for JP-8
 - DO NOT USE: butyl rubber or latex (surgical gloves)
- Cotton coveralls do not provide adequate barrier against fuel
 - Liquid contact with fuel and permeable to vapor issue
 - non-permeable coveralls create heat stress situations
- Protective footwear needs standardization (cannot decon JP-8 off of leather)

Sampling Methodology

- NIOSH method 1501 (GC/FID) overestimates benzene exposures in complex hydrocarbon environments



USAF Jet Fuel Program Ongoing Studies

- Acute Exposure Risk Assessment & Epidemiology
- Benzene Exposure Assessment
- Aerosol Personal Air Sampling Methods Development



JP-8 Acute Exposure Risk Assessment & Epidemiology Study

Purpose: Collect site specific acute exposure information through field industrial hygiene and epidemiology surveillance, biological specimen sampling, and neurological assessment of selected subjects groups

Start Date: July 1999

Estimated Completion Date: December 2000

Total Subject Sample Size: 340

Study Design: Cross Sectional Epidemiologic Study

Exposed Group: Aircraft Fuel Tank Workers

Unexposed Group: Matched Indigenous Base Personnel

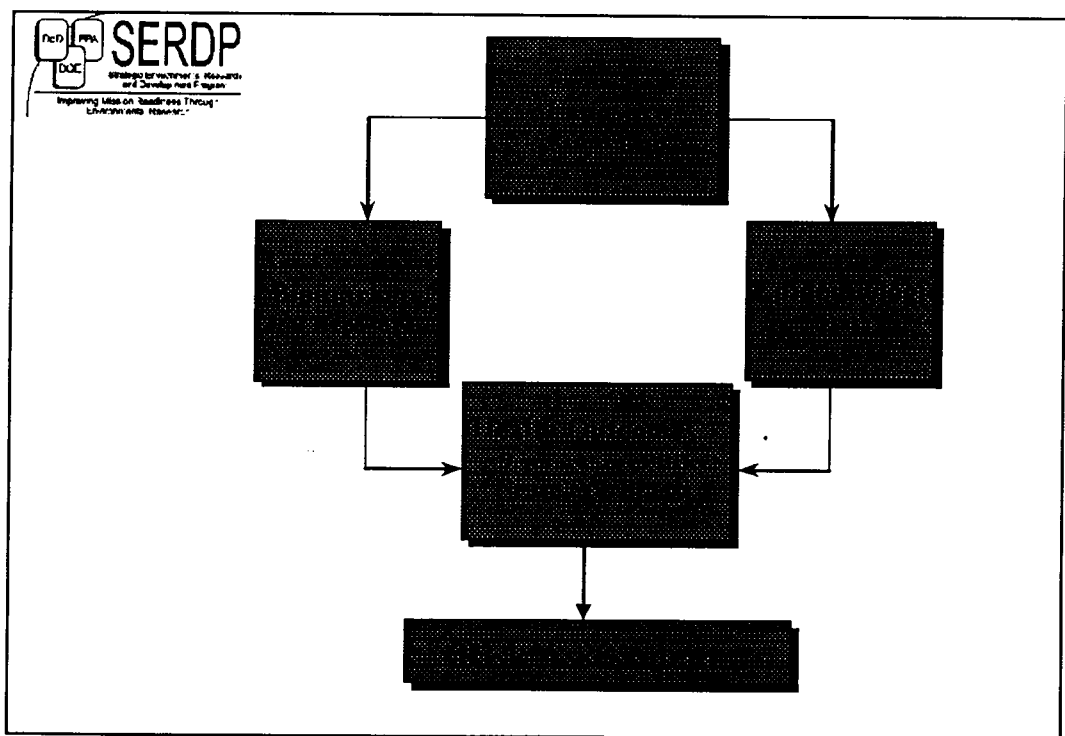
Locations: Seven Selected USAF Bases in Continental US



JP-8 Acute Exposure Risk Assessment & Epidemiology Study

Technical Objectives

- Assess acute exposure to JP-8 to better estimate safe occupational exposure levels.
- Characterize potential acute health effects associated with exposure to JP-8.
- Recommend actions to prevent/reduce exposure to JP-8.
- Conduct risk assessment for environmentally and occupationally exposed subjects.





JP-8 Acute Exposure Risk Assessment & Epidemiology Study

Outcomes

- Expected outcomes evaluated include:
 - epidemiological assessment of community
 - environmental/ambient air samples
 - biological markers of exposure
 - neurological assessment

- Neurological assessment of community will include:
 - assessment of outcomes from GST, ERG, postural sway and GASH
 - comparison of methods to assess effect of JP-8 on regions of cerebellum:
 - » vestibular
 - » visual



USAF Jet Fuel Program Future Plans

- Chronic Exposure Risk Assessment & Epidemiology
- Fate of Respirable Aerosol from Jet Engine Emissions
- Dermal Exposure Assessment
- Others:
 - Heat Stress
 - Explosive Limit Detection Technology
 - Personal Protective Issues
 - Biomarkers
 - Replacement Fuels, ...

Proposed AEGLs for Jet Propellant Fuel 8 (JP-8)

March 12, 1999

ORNL Staff Scientist:

Sylvia S. Talmage

Chemical Managers:

John Hinz,

Kenneth Still

Glenn Leach

Chemical Reviewers:

Bill Bress

William Pepelko

Robert Snyder

STATUS OF JET FUELS (JP-4, JP-5, JP-7, JP-8)

Jet propellant (JP) fuels are used in military and civilian aircraft. In the military, JP-8 is being phased in as a replacement for JP-4. JP-5, a "subset" of JP-8 is a fire-safe turbine engine fuel used by the U.S. Navy. JP-7 is/was used in reconnaissance aircraft. Both JP-5 and JP-8 are composed primarily of kerosene which is a complex mixture. These fuels are enhanced with antioxidants, dispersants, or corrosion inhibitors.

Use: 4.5 billion gallons of JP-8

Data on JP-8 are sparse to moderate
There is an abundance of data on JP-4

Jet Fuels - Toxicity

Jet Fuels are not highly acutely toxic by the inhalation route

No human deaths reported

No lethality during chronic animal exposures to JP-4 vapors at high concentrations (5000 mg/m³)

The U.S. Navy's Occupational Safety and Health standards were reviewed by the NRC/COT Subcommittee on Permissible Exposure Levels for Military Fuels. The NRC/COT recommended an 8-hour TWA of 350 mg/m³ and a 15-minute STEL of 1000 mg/m³ (reduced from 1800 mg/m³).

Renal tubular degeneration observed in male rats is unique to this species/sex and not relevant to humans

Question: Do we need to derive short-term (< 8 hour) values for chemicals of low toxicity with no apparent concentration-response data?

Jet Fuels - Toxicity

Oral route: jet fuels have low toxicities

JP-4

rat oral LD₅₀: > 5 g/kg (Clark et al., 1989)

effects: lethargy followed by recovery

rat oral LD₅₀: > 8 g/kg (MacEwen and Vernot, 1974)

JP-5

rat LD₅₀: 39, > 60 mL/kg (Bogo et al., 1982)

JP-8

rat oral LD₅₀: > 5 g/kg (Wolfe et al., 1996)

effects: lethargy and shallow breathing followed by normal appearance

JP-8 + 100

rat oral LD₅₀: > 5 g/kg (Wolfe et al., 1996)

Monitoring Data for Jet Fuels			
Fuel Type	Concentration (mg/m ³)	Exposure Duration	Reference
JP-4	33-3090 (range) 620	minutes (fueling time) 30 minutes	Martone, 1981
JP-4	< 3-3014 ^c	0.5-4 hours	Thomas and Richardson, 1981
Swedish military ^a	29-3226 (range) 300 974 925	17 years (mean) 8-hour TWA ^b 55 minutes 97 minutes	Knave et al., 1978
Swedish military	93 149 649	8-hour TWA half-day short-term	Holm et al., 1987
Swedish military	> 350	not specified	Selden and Ahlborg, 1991
Danish military	1-1020 (range) 31 (average)	up to 31 years 6.4 years (median) 4 hours (median, daily)	Døssing et al., 1985
JP-5	< 0.48-153 (range) 4.4 (mean)	TWA	NRC, 1996
JP-8	< 20	minutes (fueling time)	Martone, 1981
JP-8	0.12-2308 ^c 17-10,295 ^c	8-hour TWA 15 minute samples	Smith and Zelnick, 1998
JP-8 (mist)	10- > 200	dissipated in < 1 minute	Leith et al., 1998
JP-8 (aerosol)	16-119	minutes to hours	Rebledo and Witten, 1998

^aEquivalent to JP-4.

^bTime-weighted average.

^cSamples were taken inside aircraft fuel tanks during maintenance operations.

Jet Fuels - Vapor Inhalation Toxicity

JP-4

38,000 mg/m³ for 6 hours: rats, poor coordination (MacEwen and Vernot, 1974)
5000 mg/m³ for 4 hours: rats, no effects (Clark et al., 1989)
5000 mg/m³ for 8-12 months: rats, mice, monkeys, and dogs
initial depressed activity in monkeys and dogs
(MacEwen and Vernot, 1974; Bruner et al., 1993)

JP-5

1636 mg/m³ for 6 weeks: rats, no effects
750 mg/m³ for 90 days continuous: rats, mice, and dogs, mild liver effects
(MacEwen and Vernot, 1985; Gaworski et al., 1984, 1985)

JP-7

750 mg/m³ for 12 months: rats and mice, biochemical changes
(Kinkead et al., 1991)

JP-8

3430 mg/m³ for 4 hours: rat, eye/upper respiratory irritation (Wolfe et al., 1996)
1000 mg/m³ for 90 days continuous: rats and mice, minor biochemical changes
(MacEwen and Vernot, 1985)

Jet Fuels - Aerosol Inhalation Toxicity

JP-5

5000 mg/m³ for 1 hour: rats and mice, eye irritation and some CNS depression (MacEwen and Vernot, 1985)

JP-8

4440 mg/m³ for 4 hours: rat, eye/upper respiratory irritation (Wolfe et al., 1996)

100-2500 mg/m³ for 1 hour/7 days: mice, primarily reversible changes in spleen and thymus (Harris et al., 1997a; 1997b)

500, 1000 mg/m³ for 1 hour/7, 28, 56 days: rat, biochemical/organ weight changes, lung compliance/histology changes (Pfaff et al., 1995 and others)

28-112 mg/m³ for 1 hour: mice, lung biochemical/ultrastructural changes (Robledo and Witten, 1998)

Derivation of AEGL-1

Humans

Monitoring data: chronic no-effect concentration of $\sim 300 \text{ mg/m}^3$ for JP-4 or equivalent (Knave et al., 1978)

No uncertainty factors because we are applying a chronic exposure to an 8-hour time period and no/minor differences between individuals or among species have been demonstrated. The toxicity of JP-4 and JP-8 are similar.

Animal Study

90 day continuous no-effect exposure of rats and mice to 1000 mg/m^3 of JP-8 (MacEwen and Vernet, 1985)

No interspecies uncertainty factor because we are applying a continuous subchronic exposure to an 8-hour time period and no/minor differences between individuals or among species have been demonstrated

Adjust by intraspecies uncertainty factor of 3 to protect sensitive individuals
= $\sim 300 \text{ mg/m}^3$

Derive one 8-hour AEGL-1 value because the value is based on a long-term no-effect concentration

Derivation of AEGL-1 (con'd)

If shorter term values are needed, use additional monitoring data: (Knave et al., 1978). However, it is not clear what, if any, effects occur at these concentrations.

974 mg/m³ for 55 minutes

925 mg/m³ for 97 minutes

Use 900 mg/m³ for 1 hour value?

SUMMARY OF PROPOSED JET FUELS AEGL-1 VALUES				
Classification	Exposure Duration			
	30-Minute	1-Hour	4-Hour	8-Hour
AEGL-1 (Nondisabling)	Not determined	Not determined	Not determined	300 mg/m ³

Derivation of AEGL-2

Human data

It is assumed that the short-term exposures to $\sim 3000 \text{ mg/m}^3$ (Knave et al., 1978) were responsible for the acute symptoms observed during monitoring studies (neurotoxic effects of fatigue, headache, dizziness, nausea, palpitations, thoracic oppression, and sleep disturbances). However, no exposure durations were given.

Animal studies

Chronic exposure of mice, rats, monkeys, and dogs to 5000 mg/m^3 of JP-4 resulted in initial depressed activity in monkeys and dogs, but no histological effects in any species (MacEwen and Vernot, 1974; Bruner et al., 1993).

The 5000 mg/m^3 may be considered the threshold for narcosis

No interspecies uncertainty factor because we are applying a chronic exposure to an 8-hour time period and no/minor differences between individuals or among species have been demonstrated

Adjust by intraspecies uncertainty factor of 3 to protect sensitive individuals
= $\sim 1700 \text{ mg/m}^3$

Derivation of AEGL-2 (con'd)

Derive one 8-hour AEGL-1 value because the value is based on a long-term no-effect/threshold for narcosis

SUMMARY OF PROPOSED JET FUELS AEGL-2 VALUES				
Classification	Exposure Duration			
	30-Minute	1-Hour	4-Hour	8-Hour
AEGL-2 (Disabling)	Not determined	Not determined	Not determined	1700 mg/m ³

Supporting study:

Exposures of rats to a vapor concentration of 3430 mg/m³ of JP-8 or a vapor/aerosol concentration of 4440 mg/m³ of JP-8 for 4 hours resulted in irritation but no gross lesions at sacrifice (Wolfe et al., 1996). Because these effects are below the definition of an AEGL-2, divide by an intraspecies uncertainty factor of 2 (= 1700 or 2200 mg/m³) or by an intraspecies uncertainty factor of 3 (=1100 or 1500 mg/m³).

Derivation of AEGL-3

Human data: None

Animal Studies

Exposure of rats to the saturated vapor (38,000 mg/m³) of JP-4 for 6 hours resulted in poor coordination after 10 minutes and sporadic convulsions in several rats throughout the exposure but no deaths during the 14-day observation period (Kinkead et al., 1993)

Consider this concentration the threshold for lethality

Adjust by interspecies uncertainty factor of 3 because it is an acute study

Adjust by an intraspecies uncertainty factor of 3 to protect sensitive individuals

Use $C^n \times t$ where n is between 1 and 2 to derive 8-hour value

SUMMARY OF PROPOSED JET FUELS AEGL-3 VALUES				
Classification	Exposure Duration			
	30-Minute	1-Hour	4-Hour	8-Hour
AEGL-3 (Lethal)	Not determined	Not determined	Not determined	3000 mg/m ³

SUMMARY OF PROPOSED JET FUELS AEGL VALUES

Classification	Exposure Duration			
	30-Minute	1-Hour	4-Hour	8-Hour
AEGL-1 (Nondisabling)	Not determined	Not determined	Not determined	300 mg/m ³
AEGL-2 (Disabling)	Not determined	Not determined	Not determined	1700 mg/m ³
AEGL-3 (Lethal)	Not determined	Not determined	Not determined	3000 mg/m ³

Problems/Questions

Should this document address/include all jet fuels or just JP-8?

Do we need additional monitoring data?

Are aerosols relevant to community exposures?

Because of its relatively low vapor pressure, JP-8 might not attain a sustained vapor concentration of 3000 mg/m^3 in the environment. A concentration of 500 mg/m^3 may be the upper bound for a stable cloud of inhalable dust or aerosol.

Do we have additional safety by basing some/all of the JP-8 AEGL values on the more volatile JP-4?

Do we need to derive short-term (< 8 hour) values for chemicals of low toxicity with no apparent concentration-response data?

Sulfur Tetrafluoride



March 12, 1999

Staff Scientist:

Chemical Manager:

Chemical Reviewers:

Dr. Carol Forsyth

Mr. Kyle Blackman

Dr. Zarena Post

Dr. James Holler

Bottom Line on SF₄:

Can not establish AEGL values with any confidence

Insufficient Toxicity Data on SF₄

Insufficient Data on Possible Interactions of HF and H₂SO₄

Data:

Human	One accident - without time or concentration
Animal	Three studies on rats without study details (Clayton, 1962) 19 ppm x 4hr x 1 exposure - one of two died 40 ppm x 1hr x 1 exposure – none died 4 ppm x 4hr x 10 exposures – reversible pulmonary damage

Other Standards:

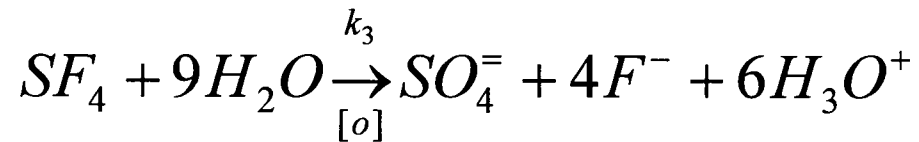
NIOSH	0.1ppm (ceiling) - derivation undocumented
ACGIH	0.1ppm (ceiling) - derivation undocumented

Result of data search:

Insufficient data for AEGL determination

Alternative Approach

Hydrolysis of SF₄ (aqueous phase)



SF₄ produces 1 mole H₂SO₄ and 4 mole HF or 6 moles of free protons

Adjust existing HF AEGL on the ratio of free protons produced ***And added modifying factor for “data base”***

Inadequacy of alternative approach:

Does not address the possible interactions of F⁻ and SO₄⁼

Committee has not set AEGL values for H₂SO₄ (may be on June Agenda)

Mechanics of Alternative Approach

Proton ratio for hydrolysis SF ₄ / HF	6
Modifying factor for “data base”	2
Total Modifying Factor	12

Calculation of AEGL:

$$\mathbf{AEGL-SF_4 = AEGL-HF / 12}$$

Alternative Approach Calculations:

AEGL-1	30 min	1 hour	4 hours	8 hours
HF (ppm)	2	2	1	1
MF	12	12	12	12
SF4 (ppm)	0.17	0.17	0.08	0.08

AEGL-2	30 min	1 hour	4 hours	8 hours
HF (ppm)	34	24	12	8.6
MF	12	12	12	12
SF4 (ppm)	2.8	2.0	1.0	0.7

AEGL-3	30 min	1 hour	4 hours	8 hours
HF (ppm)	62	44	22	15
MF	12	12	12	12
SF4 (ppm)	5.2	3.7	1.8	1.3

Limited SF₄ Data Calculations AEGL-2:

4 ppm x 4hr x 10 exposures – reversible pulmonary damage

n = 2 empirically derived for HF

C = 4 ppm

t = 240 min

UF = 10

k = 38.4

Time (min)	30	60	240	480
ppm	1.1	0.80	0.40	0.28

Limited SF₄ Data Calculations AEGL-3:

40 ppm x 1hr – “threshold for lethality”

n = 2 empirically derived for HF

C = 40 ppm

t = 60 min

UF = 10

k = 960

Time (min)	30	60	240	480
ppm	5.7	4.0	2.0	1.4

Comparisons of Approaches:

AEGL-1	30 min	1 hour	4 hours	8 hours
HF Conversion	0.17	0.17	0.08	0.08
SF ₄ in rats	- na -	- na -	- na -	- na -

AEGL-2	30 min	1 hour	4 hours	8 hours
HF Conversion	2.8	2.0	1.0	0.7
SF ₄ in rats	1.1	0.80	0.40	0.28

AEGL-3	30 min	1 hour	4 hours	8 hours
HF Conversion	5.2	3.7	1.8	1.3
SF ₄ in rats	5.7	4.0	2.0	1.4

Recommendation to the Committee:

Do Not Establish AEGL Values for SF₄

BHOPAL DISASTER

Immediate Effects:

- death
- coughing, pulmonary edema
- eye irritation, lacrimation, photophobia, corneal ulceration
- spontaneous abortion

Long-term Effects:

- cough, breathlessness, chest pain
- reduced pulmonary function
- eye irritation, reduction in vision, corneal opacity
- infant death

EFFECTS OF MIC IN ANIMALS

Death

Signs of irritation to mucus membranes

Histological lesions in lung

Decrements in pulmonary function

Litter resorption

Little species variation

HUMAN EXPOSURE DATA

Mellon Institute, 1970

Study Population: 6 volunteers

Exposure: 0.5 ppm for 10 minutes

Results:

- 6 - eye irritation**
- 5 - tearing**
- 4 - nose irritation**
- 2 - throat irritation**
- 1 - odor after 3 min**

.....

Study Population: 8 volunteers

Exposure: 1.75 ppm for 1 min

Results:

- 8 - eye irritation**
- 7 - tearing**
- 3 - nose and throat irritation**

Proposed AEGL-1 for Methyl Isocyanate

Key study: Mellon Institute, 1970

Exposure: 0.5 ppm for 10 minutes

Toxicity endpoint: eye irritation, lacrimation, nose irritation, and/or throat irritation in human volunteers

Scaling: none

Uncertainty factors: 3 - sensitive individuals

Modifying factors: 2 - short experimental duration (4- and 8-hour)

Proposed AEGL-1 Values for MIC (ppm [mg/m ³])				
	30-min	1-hr	4-hr	8-hr
AEGL-1	0.17 [0.40]	0.17 [0.40]	0.08 [0.19]	0.08 [0.19]

Supporting data:

Exposures: 1.8 ppm for 7 hours - NOEL for irritation in rats and rabbits (Dow Chemical, 1990)

1 ppm for 2 hr/day, 3 x/week, 3 weeks - no adverse effects or respiratory sensitization in guinea pigs (Mellon Institute, 1990)

ANIMAL EXPOSURE DATA

Ferguson and Alarie, 1991

Species: male guinea pig; 8/group

Exposure: 6, 13, 19, 27, or 37 ppm (analytical) for 3 hours

Results:

6 and 13 ppm: ■ no deaths

■ reversible histopathological lesions

■ reversible decrements in pulmonary function

27 ppm: ■ 8/8 died

19 and 37 ppm: ■ 2/8 and 6/8 died

■ impairment of pulmonary function at 1 year

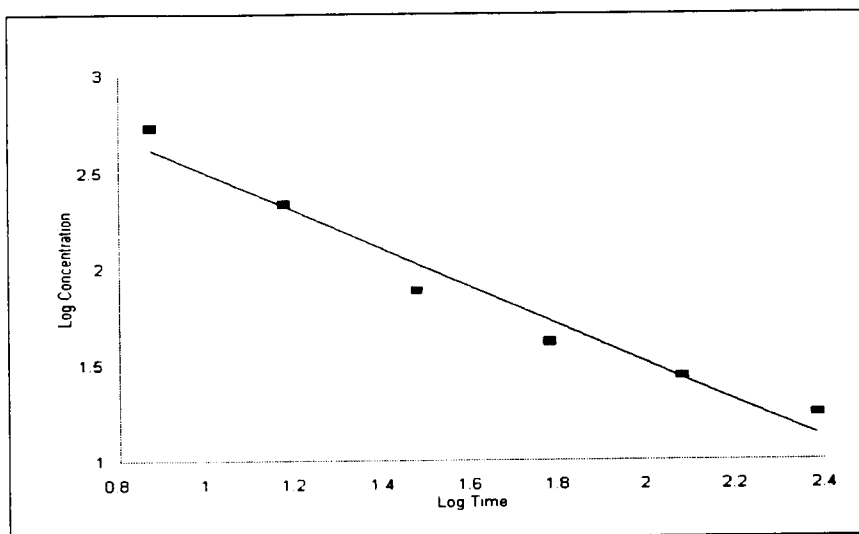
■ scarring, fibrosis, atelectasis in the lung; more pronounced at 37 ppm

DERIVATION OF n FROM RAT LC_{50} DATA

Reference: Mellon Institute, 1970

Duration	LC_{50}
7.5 min	541 ppm
15 min	216 ppm
30 min	76.6 ppm
60 min	41.3 ppm
120 min	27.4 ppm
240 min	17.5 ppm

Equation: $y = 3.48 - 1.01x$
 $r^2 = 0.9642$
 $n = 1.01$



Proposed AEGL-2 for Methyl Isocyanate

Key study: Ferguson and Alarie, 1991

Exposure: 6 ppm for 3 hours

Toxicity endpoint: reversible impairment of pulmonary performance and histological lesions in guinea pigs

Scaling: $C^1 \times t = k$

Uncertainty factors: 10: 3 - sensitive individuals
3 - interspecies

Proposed AEGL-2 Values for MIC (ppm [mg/m ³])				
	30-min	1-hr	4-hr	8-hr
AEGL-2	3.6 [8.4]	1.8 [4.2]	0.45 [1.1]	0.23 [0.47]

Supporting data:

Exposures: 3 ppm for 6 hours - histological lesions in rats (Mitsumori et al., 1987)

10 ppm for 2 hours - intraluminal fibrosis in rats two years after exposure (Bucher and Uraih, 1989)

Proposed AEGL-3 for Methyl Isocyanate

Key study: Ferguson and Alarie, 1991

Exposure: 13 ppm for 3 hours

Toxicity endpoint: reversible impairment of pulmonary performance and histological lesions in guinea pigs

Scaling: $C^1 \times t = k$

Uncertainty factors: 10: 3 - sensitive individuals
3 - interspecies

Proposed AEGL-3 Values for MIC (ppm [mg/m ³])				
	30-min	1-hr	4-hr	8-hr
AEGL-3	7.8 [18.3]	3.9 [9.1]	0.98 [2.3]	0.49 [1.1]

Supporting data:

Exposures: 9 ppm for 3 hours - increased resorptions in rats and mice (Varma, 1987; Varma et al., 1990)

Resulting AEGL-3 values: 5.4, 2.7, 0.68, and 0.34 ppm

Summary of Proposed AEGL Values (ppm [mg/m³])

AEGL Level	30-minute	1-hour	4-hour	8-hour
AEGL-1	0.17 [0.40]	0.17 [0.40]	0.08 [0.19]	0.08 [0.19]
AEGL-2	3.6 [8.4]	1.8 [4.2]	0.45 [1.1]	0.23 [0.47]
AEGL-3	7.8 [18.3]	3.9 [9.1]	0.98 [2.3]	0.49 [1.1]

ACGIH TLV-TWA: 0.02 ppm (0.047 mg/m³) [skin] (ACGIH, 1991; 1998)

NIOSH TWA: 0.02 ppm (0.047 mg/m³) [skin]; IDLH = 3 ppm (NIOSH, 1994; 1997; based on Kimmerle and Eben, 1964)

OSHA TWA: 0.02 ppm (0.047 mg/m³) [skin] (OSHA, 1995)

ERPG levels 1, 2, and 3 are 0.025 ppm, 0.5 ppm, and 5 ppm, respectively (AIHA, 1998)

**NATIONAL ADVISORY COMMITTEE (NAC)
FOR ACUTE EXPOSURE GUIDELINE LEVELS (AEGLs)
FOR HAZARDOUS SUBSTANCES**

**Final Meeting 12 Highlights
Governor's House Hotel
1615 Rhode Island Avenue
Washington, D.C.**

December 7-9, 1998

INTRODUCTION

George Rusch (NAC Chairman) opened the meeting and welcomed all participants. Attached are the meeting agenda (Attachment 1) and the attendee list (Attachment 2).

Roger Garrett (Program Director) reported on his meeting in Europe with the Organisation for Economic Co-Operation and Development (OECD) which represents 21 nations. There is potential interest by OECD in adopting AEGL values. An observer sent by Germany, Dr. Ursula Stephan of the Hazardous Incident Commission, was welcomed by the NAC. OECD may send observers to future meetings. In further discussion, it was decided to solicit data from and use the expertise of OECD members before completion of the Technical Support Documents. However, the documents would not be sent out before adoption of values by the NAC. Roger will seek a contact person for getting information. There is a possibility of a more definitive presentation of the AEGL project to the OECD in June 1999.

Roger Garrett and Ernest Falke reported on the presentations of the Standing Operating Procedures (SOPs) and the first eight AEGLs to the National Academy of Sciences/Committee on Toxicology, Subcommittee for AEGLs. Although a formal response has not been received, the initial response from the Academy members concerning the SOPs, Technical Support Documents (TSDs), and methodology in general was positive, even where the Academy's approach to setting guidelines differed. The Academy noted that the SOP document went further than previous guideline documents. The TSDs were complimented and the response to time-scaling was especially positive. The next 10 chemicals have been sent to the Academy for their consideration. Ernie Falke noted the need to document the rationale for the uncertainty factors of 3 and 10 in the SOP. The discussion of the cancer endpoint needs additional work, but the risk of 10^{-4} is acceptable. Susceptible populations also need to be further defined in regard to the interspecies uncertainty factor issue.

Concerning additional funding, Paul Tobin and Richard Niemeier discussed the NIOSH National Occupational Research Agenda (NORA), a partnership between government, industry, and academia which funds special risk assessment projects. Paul Tobin has contacted the chairman of the NORA committee. The question arose as to whether or not a federal agency can submit a proposal. A discussion ensued concerning developmental/reproductive toxicity and the lack of human data.

Bill Pepelko said that his office is looking at differences in sensitivity between children and adults. Paul Tobin reported that interim TSDs will be accessible on the EPA Web site. The NAC/AEGL Meeting 11 highlights were reviewed and accepted unanimously following minor revisions (Appendix A).

TECHNICAL DISCUSSIONS

Definition of Ceiling Values. Problems with the definition of ceiling values were brought up by John Morawetz. Specifically, the present definition would allow multiple exposures to higher values within the longer term exposure durations. John illustrated his concern with examples of the variability of exposure concentrations during industrial monitoring and/or an accidental release (Attachment 3). If a time-weighted average is used, higher-than-ceiling values may occur during an incident. Additional language to clarify the definition of ceiling value was proposed by George Rusch. Two solutions were suggested: (1) define each point on the line connecting the four exposure durations as a ceiling, with the 30-min value flatlined to the ordinate, and (2) use the line as a continuum with concentrations for exposure durations other than the four defined times read off the line. One committee member suggested clarifying the definition of ceiling value by adding a graph to each TSD. Bob Snyder pointed out that it is important to consider the mechanism of action for each chemical.

Action Item: Ernie Falke will write up a definition of ceiling value for the SOPs document and present it to the NAC/AEGL at the next meeting.

Definition of AEGL-1 Level. The disconnect between the definition of an AEGL-1 (generally a sensory response) and the AEGL-2 and -3 (health responses) was discussed. The endpoint for the AEGL-1 has been chemical-specific and/or dependent on the data, with a hierarchical or decision tree used for: sensory irritation, biochemical response, no effect, and odor. Discussion revolved around combining all endpoints into the definition; e.g., uncertainty in the use of a NOAEL, addition of the odor threshold to the summary table, the relationship between odor and discomfort, and anxiety, and the influence of the "quality" of the odor. It was noted that several members of the National Academy of Sciences committee recommended development of an AEGL-1 even in the absence of data or when odor is above the effect level. The OECD agrees with establishment of an AEGL-1 level in the absence of data.

Action Item: Ernie Falke will compile the data on the AEGL-1 endpoints used up to this point and report back at the next meeting.

Categorical Regression. Judy Strickland of the National Center for Environmental Assessment (NCEA/USEPA) started her discussion with an overview of the development of Acute Reference Exposures (ARE). The ARE are airborne concentrations that are unlikely to cause adverse effects in a sensitive human subpopulation during intermittent exposure or a single continuous exposure of <24 hr. The ARE support implementation of the Clean Air Act Amendments, Section 112. Depending on the available data, ARE will be developed by one of three approaches: the NOAEL approach, categorical regression, or the benchmark concentration. All three methods require dosimetric adjustment (the default is 1); categorical regression does not require a duration adjustment. Judy presented schematics of the categorical regression approach (Attachment 4) in which health effects are divided into severity categories and plotted graphically with the ordinate as log concentration and the abscissa as log exposure duration. Parallel lines that separate the severity categories are then generated. All available data is used in this approach. The line defining a 10% probability of an adverse effect

with 95% confidence limits is used as the endpoint. Ernest Falke pointed out that a 10% response may be too large; whereas application of several uncertainty factors may be too conservative. The EPA Science Advisory Board reviewed the categorical regression model, agreeing with several concepts (categorizing of data, use of all data, graphical representation) and questioning several points (appropriateness of parallelism of probability-response curves for all severity categories, judging severity categories across various target organs and species, reliability of the confidence limits, and the scaling factor). The NCEA has replied to these comments as well as those that addressed the NOAEL and Benchmark approach. It was noted by a NAC/AEGL member that the regression line may be an excellent source for estimating time scaling. Judy went on to illustrate the use of categorical regression with the hydrogen sulfide data. Her ARE values were similar to the AEGL-1 values originally proposed in the TSD (Attachment 5).

AEGL PRIORITY CHEMICALS

Propionitrile, CAS No. 107-12-0

Chemical Manager: Dr. George Rogers, University of Louisville, AAPCC

Author: Dr. Cheryl Bast, ORNL

George Rogers explained the mechanism of action of the nitriles which is based on the metabolic release of hydrogen cyanide. Cheryl Bast reviewed the data on methacrylonitrile and isobutylnitrile which were presented at the last meeting, noting the relative toxicities of these two chemicals to that of propionitrile. Cheryl then summarized the data for propionitrile (Attachment 6).

The proposed AEGL-3 values for propionitrile were based a 4-hr no-effect level for death in rats. This value of 690 ppm was divided by an interspecies uncertainty factor of 10 because the rat is not the most sensitive species and by an intraspecies uncertainty factor of 3 as effects appear to be due to cyanide and observations of human occupational exposures as well as toxicity to adult and neonatal mice suggest little individual variation. The value of n of 2.6 was based on that for cyanide in a lethality study with rats over exposure durations of 5, 15, 30, and 60 min. It was moved by Richard Niemeier and seconded by John Hinz to accept the values of 51, 39, 23, and 18 ppm for the 30-min and 1-, 4-, and 8-hr exposure durations, respectively. The motion passed unanimously (Appendix B).

Following discussion of two relevant studies, a human exposure and a developmental study with the rat, the proposed AEGL-2 was based on the human accidental exposure to 33.8 ppm for 2 hr which resulted in headache, nausea, and dizziness. The 33.8 ppm value was first divided by intraspecies and modifying factors of 3 each for a total of 10 resulting in time-scaled values of 5.8, 4.4, 2.6, and 2.0 ppm. A motion was made by George Alexeeff and seconded by Jonathan Borak to accept these values; the motion did not pass [YES: 8, NO: 14, ABSTAIN: 0]. Further discussion centered on the application of a modifying factor. To be consistent with the AEGL-3 and because the mechanism of action is based on the release of cyanide, an intraspecies uncertainty factor of 3 was applied. Because of uncertainty in the data, a modifying factor of 2 was also applied. It was moved by Loren Koller and seconded by Steven Barbee to accept the values of 9.6, 7.4, 4.3, and 3.3 ppm for the 30-min and 1, 4, and 8-hr exposure durations. The motion was accepted by the NAC/AEGL [YES: 17, NO: 5, ABSTAIN: 0] (Appendix B). Because of a lack of data, AEGL-1 values were not derived (moved, Loren Koller; seconded, Mark McClanahan). The motion passed unanimously (Appendix B).

SUMMARY OF PROPOSED AEGL VALUES FOR PROPIONITRILE					
Classification	30-Min	1-Hr	4-Hr	8-Hr	Endpoint
AEGL-1	ID	ID	ID	ID	
AEGL-2	9.6 ppm (22 mg/m ³)	7.4 ppm (17 mg/m ³)	4.3 ppm (9.8 mg/m ³)	3.3 ppm (7.6 mg/m ³)	Headache, nausea, and dizziness in human subject
AEGL-3	51 ppm (120 mg/m ³)	39 ppm (89 mg/m ³)	23 ppm (53 mg/m ³)	18 ppm (41 mg/m ³)	NOEL for death, rat

ID = Insufficient data.

Cyclohexylamine, CAS No. 108-91-8

Chemical Manager: Dr. Mark McClanahan, Centers for Disease Control and Prevention

Author: Dr. Sylvia Milanez, ORNL

Following discussion of the available data and presentation by Sylvia Milanez (Attachment 7), the discussion centered around relative species sensitivities, suitable endpoints for each AEGL level, and the deficiencies in the database. The AEGL-3 was based on the 4-hr exposure of rats to 567 ppm which was the threshold value for lethality. The value was adjusted by an interspecies uncertainty factor of 10 because there was insufficient data to determine the most sensitive animal species. Because one of two rats that died at the next higher dose had lung hemorrhage/edema, cyclohexylamine was determined to be a respiratory irritant. An intraspecies uncertainty factor of 3 was used because the mechanism of action for direct irritation by a strong base is not expected to differ among individuals. Scaling across time was based on $n = 2$. It was moved by Richard Niemeier and seconded by Bob Benson to accept the resulting values of 53, 38, 19, and 13 ppm for the 30-min, 1-, 4-, and 8-hr exposure durations, respectively. The motion passed [YES: 21, NO: 3, ABSTAIN: 0] (Appendix C).

Following a lengthy discussion on uncertainty and modifying factors and several votes, it was decided to base the AEGL-2 values on the no-effect concentration of 150 ppm for corneal opacity in rats and guinea pigs. An earlier vote included time-scaled values of 18, 13, 6.3, and 4.5 ppm based on an estimated no-effect level of 189 ppm (4 hrs) for corneal opacity in the rat with a combined uncertainty factor of 30 as for the AEGL-3 above. The motion did not pass [YES: 15, NO: 10, ABSTAIN: 0]. Although exposures to 150 ppm were repeated, the 7-hr exposure duration from the first day was chosen as the exposure time. An intraspecies uncertainty factor of 3 (cyclohexylamine is a direct acting irritant; effects are not expected to differ among individuals), an interspecies uncertainty factor of 3 (the endpoint of corneal opacity is not likely to differ greatly among species), and a modifying factor of 2 (to account for a deficient database) were applied (for a total uncertainty/modifying factor of 20); time scaling was based on $n = 2$. The NAC noted that the AEGL-2 values may cause respiratory irritation in humans. It was moved by Doan Hanson and seconded by Bob Benson to accept the resulting values of 28, 20, 9.9, and 7.0 ppm for the 30-min and 1-, 4-, and 8-hr exposure durations, respectively. The motion passed [YES: 17, NO: 7, ABSTAIN: 0] (Appendix C). It was noted by the committee that different modifying factors were applied to the AEGL-2 and AEGL-3.

The AEGL-1 was based on the LOAEL value for irritation of 54.2 ppm during a 4-hr exposure of rats

to cyclohexylamine. This value was divided by 3 to attain a NOAEL (and mild or no respiratory irritation) and by interspecies and intraspecies uncertainty factors of 3 and 3 (total 10) because cyclohexylamine is a direct-acting irritant and its effects are not likely to vary greatly among humans or between species. The resulting value of 1.8 was flatlined across all AEGL time intervals. A motion to accept this value was proposed by Steve Barbee and seconded by Bill Pepelko. The motion passed [YES: 23, NO: 1, ABSTAIN: 0] (Appendix C). The 1.8 ppm value is supported by a <20% depression in respiratory rate during exposure to 4 ppm in an RD₅₀ study with the mouse.

SUMMARY OF PROPOSED AEGL VALUES FOR CYCLOHEXYLAMINE					
Classification	30-Min	1-Hr	4-Hr	8-Hr	Endpoint
AEGL-1	1.8 ppm (7.3 mg/m ³)	1.8 ppm (7.3 mg/m ³)	1.8 ppm (7.3 mg/m ³)	1.8 ppm (7.3 mg/m ³)	NOAEL or mild respiratory irritation, rat
AEGL-2	28 ppm (114 mg/m ³)	20 ppm (81 mg/m ³)	9.9 ppm (40 mg/m ³)	7.0 ppm (28 mg/m ³)	NOAEL for corneal opacity, rat. May cause respiratory irritation in humans.
AEGL-3	53 ppm (217 mg/m ³)	38 ppm (153 mg/m ³)	19 ppm (77 mg/m ³)	13 ppm (54 mg/m ³)	Threshold for lethality, rat

Hydrogen sulfide, CAS No. 7783-06-4

Chemical Manager: Dr. Steven Barbee, Arch Chemical Co.

Author: Dr. Cheryl Bast, ORNL

Following an introduction by Steven Barbee, Cheryl Bast presented an overview of the human and animal data and the relatively high value of *n* based on several of the data sets (Attachment 8). NAC/AEGL discussions centered primarily on sources of odor, odor detection, and at what concentration the odor becomes objectionable. It was noted that human deaths have occurred, primarily in enclosed spaces. The AEGL-3 was based on a 1-hr exposure concentration of 504 ppm which was a NOEL for death in rats. This value was adjusted by an interspecies uncertainty factor of 3 (the rat is only slightly less sensitive than the mouse and the rat showed the best dose response) and an intraspecies uncertainty factor of 3 (the mechanism of action of hydrogen sulfide is well known and will not differ greatly among individuals). A value of *n* of 4.36, derived from combined rat lethality data for periods of 10 mins to 6 hr was used to scale the values across time. The resulting concentrations for the 10- and 30-min and 1-, 4-, and 8-hr exposure durations were 76, 60, 50, 37, and 31 ppm, respectively. Following a motion by Mark McClanahan which was seconded by Loren Koller, the values were accepted unanimously (Appendix D).

The AEGL-2 was based on a 4-hr exposure of rats to 200 ppm which resulted in perivascular edema and increased protein and LDH in lavage fluid. This value was divided by inter- and intraspecies uncertainty factors of 3 each and scaled across time as for the AEGL-3 above. It was moved by Loren Koller and seconded by Ernie Falke to accept the resulting values of 42, 32, 28, 20, and 17 ppm for the

10- and 30-min and 1-, 4-, and 8-hr exposure durations, respectively. The motion carried [YES: 24, NO: 1, ABSTAIN: 0] (Appendix D). References from the ACGIH and WHO reports will be provided for discussion at the next meeting.

For the AEGL-1, Cheryl presented data on a no-effect level in exercising asthmatics exposed to hydrogen sulfide. The discussion for the AEGL-1 again centered around objectionable odor and data from hot springs and hog farms was cited by committee members. It was suggested that the endpoint of uncomfortable or objectionable odor could be used as an AEGL-1 endpoint. George Alexeeff cited data indicating that 5 times the odor threshold of 0.03 ppm (0.15 ppm) is objectionable to humans. It was moved by Larry Gephart and seconded by Dave Belluck that the 0.15 ppm concentration, flatlined across time, be accepted as the AEGL-1. The motion passed unanimously (Appendix D).

In addition to providing a reference from the ACGIH document, the committee asked that the primary reference cited by George Alexeeff on objectionable odor be provided at the next meeting. The committee also noted that the same odor problem exists with methyl mercaptan and suggested revisiting this chemical at the next meeting.

SUMMARY OF PROPOSED AEGL VALUES FOR HYDROGEN SULFIDE						
Classification	10-Min	30-Min	1-Hr	4-Hr	8-Hr	Endpoint
AEGL-1	Not derived	0.15 ppm (0.21 mg/m ³)	0.15 ppm (0.21 mg/m ³)	0.15 ppm (0.21 mg/m ³)	0.15 ppm (0.21 mg/m ³)	Objectionable odor, humans
AEGL-2	42 ppm (59 mg/m ³)	32 ppm (45 mg/m ³)	28 ppm (39 mg/m ³)	20 ppm (28 mg/m ³)	17 ppm (24 mg/m ³)	Lung edema, rat
AEGL-3	76 ppm (106 mg/m ³)	60 ppm (85 mg/m ³)	50 ppm (71 mg/m ³)	37 ppm (52 mg/m ³)	31 ppm (44 mg/m ³)	NOEL for death, rat

1,1,1,2-Tetrafluoroethane (HFC-134a), CAS No. 811-97-2

Chemical Manager: Dr. George Rusch, AlliedSignal, Inc.

Author: Dr. Sylvia Talmage, ORNL

George Rusch is the NAC/AEGL Chair and Chemical Managers (CM) for HFC-134a and HCFC-141b. He opened the discussion on these chemicals with remarks to delineate his technical contributions and his NAC/AEGL responsibility. George is the Director of Risk Assessment and Toxicology of AlliedSignal, Inc. In this capacity he is in charge of AlliedSignal's testing program for replacements for chlorofluorocarbons and also has served as chair of the International Program for Alternative Fluorocarbon Toxicity Testing. George contributes his technical expertise to the preparation of AEGL documents. He led the technical discussion sessions in dual roles as a Chair and as a CM. He abstained from voting on all levels of toxicity values derived from NAC/AEGL deliveries. Then, George proceeded to provide an overview of the protocol of the cardiac sensitization test with beagle dogs and the mechanism of action of chemically-induced heart arrhythmias (Attachment 9). Sylvia Talmage presented data on the first of

two halocarbons that are being considered for replacement of chlorofluorocarbons. She presented an overview of the available data, noting the richness of the database, and the development of the draft values for this chemical (Attachment 10). The AEGL-1 was based on a study with human subjects in which exposures to concentrations up to 8000 ppm for 1 hr resulted in no effects. Because this concentration is so far below concentrations showing any effects in animal studies (81,000 ppm was a no-effect concentration), the value was adjusted by an intraspecies uncertainty factor of 1. Because blood concentrations approached equilibrium by 55 min of exposure, no greater effects are anticipated at longer exposure intervals and the value of 8000 ppm was flatlined across time. There was one motion with individual votes for each AEGL level that the values be accepted. George Rogers moved and Kyle Blackman seconded the motion. The motion for the AEGL-1 passed [YES: 23, NO: 1, ABSTAIN: 2] (Appendix E). It was suggested that a statement indicating that in regard to the 10-min cardiac sensitization test, the dog is no more sensitive after 8 hr of exposure to halocarbons be added to the TSD.

The AEGL-2 was based on the no-effect concentration of 40,000 ppm in a cardiac sensitization test with beagle dogs in which the doses of epinephrine were individualized to each dog. Because the dog is a good model for the human in this test, an interspecies uncertainty factor of 1 was applied. Because the test is optimized with administration of greater than a physiological dose of epinephrine and differences among individuals are not anticipated, the value was adjusted by an intraspecies uncertainty factor of 3. Because exposure durations do not influence the results of the test, the resulting value of 13,000 ppm was flatlined across time. It was noted that other endpoints, such as the threshold for narcosis of 200,000 ppm in several animal species, when divided by inter- and intraspecies uncertainty factors of 3 each, would result in a higher value for the AEGL-2. The value for the AEGL-2 passed unanimously, with George Rusch abstaining (Appendix E).

The AEGL-3 value was based on a concentration of 80,000 ppm which resulted in a marked response in two of six dogs in the cardiac sensitization test. The next higher dose of 160,000 ppm resulted in convulsions in one of four dogs. Using the same reasoning as for the AEGL-2 above, the value of 27,000 ppm (80,000 ppm/3) was proposed for all AEGL-3 exposure durations. The value for the AEGL-3 passed [YES: 25, NO: 0, ABSTAIN: 1] (Appendix E). It was pointed out that other endpoints, such as the threshold for lethality of 359,000 ppm in an animal study, would, when divided by inter- and intraspecies uncertainty factors of 3 each, result in a higher value for the AEGL-3.

SUMMARY OF PROPOSED AEGL VALUES FOR 1,1,1,2-TETRAFLUOROETHANE					
Classification	30-Min	1-Hr	4-Hr	8-Hr	Endpoint
AEGL-1	8000 ppm (34,000 mg/m ³)	8000 ppm (34,000 mg/m ³)	8000 ppm (34,000 mg/m ³)	8000 ppm (34,000 mg/m ³)	No effects, humans (Emmen and Hoogendijk, 1998)

AEGL-2	13,000 ppm (55,250 mg/m ³)	13,000 ppm (55,250 mg/m ³)	13,000 ppm (55,250 mg/m ³)	13,000 ppm (55,250 mg/m ³)	No effect in cardiac sensitization test with dogs (Hardy et al., 1991)
AEGL-3	27,000 ppm (114,750 mg/m ³)	27,000 ppm (114,750 mg/m ³)	27,000 ppm (114,750 mg/m ³)	27,000 ppm (114,750 mg/m ³)	Marked response in cardiac sensitization test with dogs (Hardy et al., 1991)

1,1-Dichloro-1-fluoroethane (HCFC-141b), CAS No. 1717-00-6

Chemical Manager: Dr. George Rusch, AlliedSignal, Inc.

Author: Dr. Sylvia Talmage, ORNL

Sylvia Talmage reviewed the data and noted corrections in the results of the dog sensitization test made necessary by receipt of primary references from a chemical company (Attachment 11). It was noted that HCFC-141b is more toxic than HFC-134a and takes longer to reach equilibrium in the blood than HFC-134a. The AEGL-1 was based on a 4-hr no-effect concentration of 1000 ppm in a study with exercising human subjects. Because no individual differences were noted in the study and because this concentration is far below the highest no-effect concentration in animal studies of 30,000 ppm, it was adjusted by an intraspecies uncertainty factor of 1. Because blood concentrations in this same study approached equilibrium by 145 min and effects are thought to be determined by blood concentrations, the value of 1000 ppm was flatlined across all AEGL-1 time periods. It was moved by Mark McClanahan and seconded by Richard Niemeier to accept all AEGL values. The motion passed with individual values for the AEGL-1 of YES: 21, NO: 0, ABSTAIN: 2 (Appendix F). This value is supported by the NOEL value of 2600 ppm in a cardiac sensitization test with the beagle dog.

The AEGL-2 was based on a concentration of 5200 ppm which caused a marked response in one of ten beagle dogs in one of two cardiac sensitization tests. A single high dose of epinephrine was administered to each dog in this study (8 µg/kg), i.e., doses were not individualized for each dog. Because the dog is a good model for the human in this test, an interspecies uncertainty factor of 1 was applied. Because the test is optimized with administration of greater than a physiological dose of epinephrine and great differences among individuals are not anticipated, the value was adjusted by an intraspecies uncertainty factor of 3. Because exposure durations do not influence the results of the test, the resulting value of 1700 ppm was flatlined across time. The previously made motion to accept the AEGL values by Mark McClanahan and seconded by Richard Niemeier passed with individual votes for the AEGL-2 [YES: 22, NO: 0, ABSTAIN: 1] (Appendix F). George Rogers pointed out that in the human study this chemical does not reach equilibrium in the blood within the 10-min test time period used in the cardiac sensitization test. It was also noted that other endpoints, such as the threshold for narcosis of 30,000 ppm in mice when divided by inter- and intraspecies uncertainty factors of 3 each would result in a higher value for the AEGL-2.

The AEGL-3 value was based on a concentration of 9000 ppm which resulted in a marked response in one of two dogs in a cardiac sensitization test. In this study, the highest nonlethal concentration was 19,000 ppm; however in an earlier cardiac sensitization test, one of ten dogs exposed to 10,000 ppm died. Therefore, 9000 ppm was considered the threshold for lethality. Using the same reasoning as for the AEGL-2 above, the value of 9000 ppm was divided by 3 and flatlined for all AEGL-2 exposure

durations. The previously made motion by Mark McClanahan which was seconded by Richard Niemeier to accept the proposed values passed with individual votes for the AEGL-3 [YES: 22, NO: 0, ABSTAIN: 1] (Appendix F). It was pointed out that other endpoints, such as the highest nonlethal concentration in the absence of an exogenous dose of epinephrine of 45,781 ppm in an animal study, would, when divided by inter- and intraspecies uncertainty factors of 3 each, result in a higher value for the AEGL-3.

SUMMARY OF PROPOSED AEGL VALUES FOR 1,1-DICHLORO-1-FLUOROETHANE					
Classification	30-Min	1-Hr	4-Hr	8-Hr	Endpoint
AEGL-1	1000 ppm (4850 mg/m ³)	1000 ppm (4850 mg/m ³)	1000 ppm (4850 mg/m ³)	1000 ppm (4850 mg/m ³)	No effects, humans (Utell et al., 1997)
AEGL-2	1700 ppm (8245 mg/m ³)	1700 ppm (8245 mg/m ³)	1700 ppm (8245 mg/m ³)	1700 ppm (8245 mg/m ³)	Marked response, cardiac sensitization test, dogs (1/10)
AEGL-3	3000 ppm (14,550 mg/m ³)	3000 ppm (14,550 mg/m ³)	3000 ppm (14,550 mg/m ³)	3000 ppm (14,550 mg/m ³)	Highest nonlethal concentration, cardiac sensitization test, dogs (Hardy et al., 1989a)

Ethylene Oxide, CAS NO. 75-21-8

Chemical Manager: Dr. Kyle Blackman, FEMA

Author: Dr. Kowetha Davidson, ORNL

Kyle Blackman reported that ethylene oxide will be revisited at the next meeting. Bill Snellings of Union Carbide Corporation, who was present at the meeting, will look for more data.

Piperidine, CAS No. 110-89-4

Chemical Manager: Dr. Mark McClanahan, Centers for Disease Control and Prevention

Author: Dr. Kowetha Davidson, ORNL

The chemical information was summarized by Mark McClanahan who noted the paucity of data for lethality and time scaling. Only an AEGL-1 had been proposed in the draft TSD. The Committee discussed the available lethality data and considered the data adequate to derive an AEGL-3. The Committee based the AEGL-3 on a reported 4-hr LC₅₀ of 1723 ppm for the mouse (Attachment 12). This value was divided by 3 to attain a nonlethal concentration and then adjusted by an interspecies

uncertainty factor of 10 because there is only one data set and an intraspecies uncertainty factor of 3 because it is a strong primary irritant and there would be little intraspecies variation. The value of $n = 2$ was used for time scaling. The resulting AEGL-3 values of 54, 38, 19, and 14 ppm for the 30-min and 1-, 4-, and 8-hr time periods were accepted by the Committee (motion by Richard Niemeier, seconded by Larry Gephart [YES: 19, NO: 4, ABSTAIN: 0] (Appendix G). It was noted that the LC_{50} value on which the AEGL-3 is based was reported in a secondary source. Data that might be considered for development of an AEGL-2 were also reported in a secondary source. Further discussion on this chemical was tabled until requisition of possible primary references can be attempted.

SUMMARY OF PROPOSED AEGL VALUES FOR PIPERIDINE					
Classification	30-Min	1-Hr	4-Hr	8-Hr	Endpoint
AEGL-3	54 ppm (186 mg/m ³)	38 ppm (131 mg/m ³)	19 ppm (66 mg/m ³)	14 ppm (48 mg/m ³)	Threshold for lethality, mouse

Furan, CAS No. 110-00-9

Chemical Manager: Dr. George Rogers, University of Louisville (AAPCC)

Author: Dr. Claudia M. Troxel, ORNL

Claudia Troxel opened the discussion with a resolution of the conflicting data in mouse and rat LC_{50} studies, noting that the mouse data should be discredited based on the probability of insufficient oxygen in the closed system in which they were tested (Attachment 13). Claudia further discussed the sparse database, uncertainty factors, relative species metabolism, and mechanism of action of this chemical. The proposed AEGL-2 and -3 values were based on the 1-hr threshold for adverse effects and the threshold for lethality (highest NOEL for death) of 1014 and 2851 ppm, respectively. These values were adjusted by an interspecies uncertainty factor of 10 (although the simulated absorbed dose in the liver in humans is lower than in mice and rats, the relative species sensitivity to the reactive metabolite is unknown, and the liver was the only organ investigated), an intraspecies uncertainty factor of 3 (inter-individual variations in the activating enzyme are not predicted to be a factor in bioactivation), and by a modifying factor of 3 (sparse data set: only one study in one species). The value of $n = 2$ was used for time scaling. The proposed AEGL-2 and AEGL-3 values for the 30-min and 1-, 4-, and 8-hr time periods were 40, 29, 14, and 10 ppm and 14, 10, 5.1, and 3.6 ppm, respectively. A motion was made by Robert Snyder and seconded by Richard Thomas to accept the AEGL-2 and AEGL-3 values. The motion for both levels was accepted [YES: 19; NO: 5, ABSTAIN: 0] (Appendix H). The Committee unanimously agreed not to set AEGL-1 levels because of insufficient data.

SUMMARY OF PROPOSED AEGL VALUES FOR FURAN					
Classification	30-Min	1-Hr	4-Hr	8-Hr	Endpoint
AEGL-1	ID	ID	ID	ID	

AEGL-2	14 ppm (39 mg/m ³)	10 ppm (28 mg/m ³)	5.1 ppm (14 mg/m ³)	3.6 ppm (10 mg/m ³)	Threshold for adverse effects, rat
AEGL-3	40 ppm (110 mg/m ³)	29 ppm (81 mg/m ³)	14 ppm (39 mg/m ³)	10 ppm (28 mg/m ³)	Threshold for lethality, rat

ID = Insufficient data.

Propylene Oxide, CAS No. 75-56-9

Chemical Manager: Dr. Jim Holler, ATSDR

Author: Dr. Claudia M. Troxel, ORNL

Following a review of the history of propylene oxide presentations, human data (the data from environmental health surveys made available by the CMA) and pertinent animal data (Attachment 14) were discussed by Claudia. James Swenberg (University of North Carolina) discussed the formation of DNA adducts in the nasal tissues, tissue partition coefficients for various species, and cell proliferation of rats exposed to 500 ppm, 6 hr/day for 5 days/week (Attachment 15). Additionally, based on toxicokinetics, lethality, and pharmacokinetic modeling, the mouse is predicted to be more sensitive than humans. Therefore, there is no need for an interspecies uncertainty factor if using the mouse data for AEGL derivations. Dr. Larry Andrews of the CMA Propylene Oxide Panel expressed concern that the AEGL-3 values do not correlate with the human data (Attachment 16).

The environmental health surveys made available by the CMA were judged satisfactory by the Committee to derive all three AEGL levels. The AEGL-3 was based on the highest documented nonlethal exposure concentration of 1520 ppm for 171 min. This value was adjusted by an uncertainty factor of 3 for intraspecies differences (the mechanism of action, irritation, is not expected to differ among individuals) and by a modifying factor of 2 for a limited database (1 sample measurement from one worker; old survey) and time scaled using an *n* of 1.2 based on ethylene oxide. A motion to accept the resulting values of 1100, 610, 190, and 110 ppm for the 30-min and 1-, 4-, and 8-hr time periods was made by Jim Holler and seconded by Larry Gephart. The motion passed [YES: 19, NO: 4, ABSTAIN: 0] (Appendix I).

The AEGL-2 was based on the average of AEGL-2 values derived using four propylene oxide exposure concentrations measured in the breathing zone of three workers (see table below). At these concentrations, a strong odor with undefined irritation was reported. The AEGL-2 values were divided by an intraspecies uncertainty factor of 3 and scaled to the relevant time periods using *n* = 1.2.

EXPOSURE CONCENTRATIONS OF PROPYLENE OXIDE (ppm) MEASURED IN 3 WORKERS DURING ENVIRONMENTAL HEALTH SURVEY					
Concentration/Time	UF/MF	30-Min	1-Hr	4-Hr	8-Hr
380 ppm for 177 min.	3	560	310	98	55
525 ppm for 121 min.	3	560	310	99	56

392 ppm for 135 min.	3	460	260	81	45
460 ppm for 116 min.	3	470	270	84	47
Average	3	510	290	91	51

A motion to accept the resulting values of 510, 290, 91, and 51 ppm for the 30-min and 1-, 4-, and 8-hr time periods was made by Bill Bress and seconded by Loren Koller. The motion was unanimously passed (Appendix I).

The AEGL-1 was based on the highest 8-hr time-weighted concentration of 31.8 ppm (2 samples from 2 workers; 78 employees potentially exposed to 13.2 to 31.8 ppm). This value was divided by an intraspecies uncertainty factor of 3 (the mechanism of action, irritation, is not expected to differ among individuals) and scaled to the relevant time periods using the value of $n = 1.2$ which is based on ethylene oxide. A motion to accept the resulting values of 110, 60, 19, and 11 ppm for the 30-min and 1-, 4-, and 8-hr time periods was made by George Rogers and seconded by Richard Thomas. The motion passed [YES: 14, NO: 5, ABSTAIN: 0] (Appendix I).

SUMMARY OF PROPOSED AEGL VALUES FOR PROPYLENE OXIDE					
Classification	30-Min	1-Hr	4-Hr	8-Hr	Endpoint
AEGL-1	110 ppm (260 mg/m ³)	60 ppm (140 mg/m ³)	19 ppm (45 mg/m ³)	11 ppm (26 mg/m ³)	No effects, humans
AEGL-2	510 ppm (1200 mg/m ³)	290 ppm (690 mg/m ³)	91 ppm (220 mg/m ³)	51 ppm (120 mg/m ³)	Strong odor, irritation in monitoring study, humans
AEGL-3	1100 ppm (2600 mg/m ³)	610 ppm (1400 mg/m ³)	190 ppm (450 mg/m ³)	110 ppm (260 mg/m ³)	Highest nonlethal concentration, humans

ADMINISTRATIVE ISSUES

Times and places for the next meeting were discussed. Several options for the March meeting were prioritized with the highest priority being given to a meeting in New Orleans to precede the Society of Toxicology meeting of March 14-18.

Suggested future meetings:

- March 11-12, 1999, New Orleans, LA
or March 3-5, Washington, DC
- June 14-16, 1999, Washington, DC
- September 14-16, 1999, Washington, DC
- December 6-8, 1999, Washington, DC

George Rusch expressed appreciation for a productive meeting.

This report was prepared by Drs. Sylvia Talmage and Po-Yung Lu, ORNL.

LIST OF ATTACHMENTS

The attachments were distributed during the meeting and will be filed in the EPA Docket Office.

1. NAC/AEGL Meeting No. 12 Agenda
2. NAC/AEGL Meeting No. 12 Attendee List

3. Examples of “ceiling value” interpretations - John Morawetz
4. Use of Categorical Regression to Determine c x t Relationship for Hydrogen Sulfide - Judy A. Strickland
5. Comparison of ARE and AEGL values of Hydrogen sulfide - Judy Strickland
6. Data analysis of Propionitrile - Cheryl Bast
7. Data analysis of Cyclohexylamine - Sylvia Milanez
8. Data analysis of Hydrogen sulfide - Cheryl Bast
9. Overview of HCFC - George Rusch
10. Data analysis of HFC-134a - Sylvia Talmage
11. Data analysis of HCFC-141b - Sylvia Talmage
12. Data analysis of Piperidine - Kowetha Davidson/Mark McClanaham
13. Data analysis of Furan - Claudia M. Troxel
14. Data analysis of Propylene oxide - Claudia Troxel
15. Data analysis of Propylene oxide (DNA adducts) - James Swenberg
16. Data analysis of Propylene oxide - Larry Andrews

LIST OF APPENDICES

- A. Approved NAC/AEGL-11 Meeting Highlights
- B. Ballot for Propionitrile
- C. Ballot for Cyclohexylamine
- D. Ballot for Hydrogen sulfide
- E. Ballot for HFC -134a
- F. Ballot for HCFC 141b
- G. Ballot for Piperidine
- H. Ballot for Furan
- I. Ballot for Propylene oxide

(107-15-3)

Date of NAC/AEGL Meeting: 3/11-12/99

Chemical: Ethylene Diamine

NAC Member	AEGL 1	AEGL 2	AEGL 3	NAC Member	AEGL 1	AEGL 2	AEGL 3
George Alexeeff	Y	Y	Y	Loren Koller	Y	Y	Y
Steven Barbee	Y	Y	Y	Glenn Leach	Y	Y	Y
Lynn Beasley	Y	Y	Y	Mark A. McClanahan	Y	Y	Y
David Belluck	Y	Y	Y	John S. Morawetz	Y	Y	Y
Robert Benson	Y	N	N	Deirdre L. Murphy	Absent	Absent	Absent
Kyle Blackman	Y	Y	Y	Richard W. Niemeier	Absent	Absent	Absent
Jonathan Borak	Absent	Absent	Absent	William Pepelko	Y	Y	Y
William Bress	Y	Y	Y	Zarena Post	Absent	Absent	Absent
Luz Claudio	Y	Y	Y	George Rodgers	Y	Y	Y
George Cushmac	Y	Y	Y	George Rusch, Chair	Y	Y	Y
Ernest Falke	Y	Y	Y	Michelle Schaper	Absent	Absent	Absent
Larry Gephart	Y	Y	N	Bob Snyder	Y	Y	Y
John Hinz	Y	A	Y	Thomas Sobotka	Absent	Absent	Absent
Jim Holler	Y	Y	Y	Kenneth Still	Y	Y	Y
Thomas C. Hornshaw	Y	Y	Y	Patricia Ann Talcott	Absent	Absent	Absent
Nancy Kim	Absent	Absent	Absent	Richard Thomas	Y	Y	Y
				Thomas Tuccinardi/ Doan Hansen	A Y	A Y	A Y
				TALLY	26/26	24/25	24/26

PPM (mg/m ³)	30 Min	60 Min	4 Hr	8Hr
AEGL 1	N/A , ()	N/A , ()	N/A , ()	N/A , ()
AEGL 2	22 , ()	16 , ()	7.8 , ()	5.5 , ()
AEGL 3	49 , ()	35 , ()	17 , ()	12 , ()

N/A = Insufficient Data

AEGL 1 Motion: R. Benson Second: E. Falke

AEGL 2 Motion: S. Barbee Second: L. Koller

AEGL 3 Motion: E. Falke Second: R. Thomas

Approved by Chair: [Signature] DFO: Paul S. Volin Date: 3/11/99

(7719-12-2)

Date of NAC/AEGL Meeting: 3/11-12/99

Chemical: PHOSPHORUS TRICHLORIDE

NAC Member	AEGL 1	AEGL 2	AEGL 3	NAC Member	AEGL 1	AEGL 2	AEGL 3
George Alexeeff	Y	Y	N	Loren Koller	Y	Y	N
Steven Barbee	Y	Y	Y	Glenn Leach	Y	Y	Y
Lynn Beasley	Y	Y	Y	Mark A. McClanahan	Y	Y	Y
David Belluck	Y	Y	N	John S. Morawetz	Y	Y	Y
Robert Benson	Y	Y	Y	Deirdre L. Murphy	Absent	Absent	Absent
Kyle Blackman	Y	Y	N	Richard W. Niemeier	Absent	Absent	Absent
Jonathan Borak	A	A	A	William Pepelko	Y	Y	Y
William Bress	Y	Y	Y	Zarena Post	Absent	Absent	Absent
Luz Claudio	A	A	Y	George Rodgers	Y	Y	Y
George Cushmac	Y	Y	Y	George Rusch, Chair	Y	Y	Y
Ernest Falke	Y	Y	Y	Michelle Schaper	Absent	Absent	Absent
Larry Gephart	Y	Y	Y	Bob Snyder	Y	Y	Y
John Hinz	Y	Y	N	Thomas Sobotka	Absent	Absent	Absent
Jim Holler	Y	Y	Y	Kenneth Still	Y	Y	Y
Thomas C. Hornshaw	Y	Y	Y	Patricia Ann Talcott	Absent	Absent	Absent
Nancy Kim	A	A	A	Richard Thomas	Y	Y	N
				Thomas Tuccinardi/ Doan Hansen	A Y	A Y	A N
				TALLY	25/25	25/25	18/26

PPM, (mg/m ³)	30 Min	60 Min	4 Hr	8Hr
AEGL 1	N/A , ()	N/A , ()	N/A , ()	N/A , ()
AEGL 2	N/A , ()	N/A , ()	N/A , ()	N/A , ()
AEGL 3	1.6 , ()	1.1 , ()	0.56 , ()	0.39 , ()

*N/A = Insufficient Data

AEGL 1 Motion: D. Belluck Second: K. Blackman

AEGL 2 Motion: D. Belluck Second: K. Blackman

AEGL 3 Motion: R. Benson Second: W. Pepelko

Approved by Chair: [Signature] DFO: Paul S. Tobin Date: 3/11/99

(10025-87-3)

Date of NAC/AEGL Meeting: 3/11-12/99

Chemical: PHOSPHORUS OXYCHLORIDE

NAC Member	AEGL 1	AEGL 2	AEGL 3	NAC Member	AEGL 1	AEGL 2	AEGL 3
George Alexeeff	Y	Y	N	Loren Koller	Y	Y	Y
Steven Barbee	Y	Y	Y	Glenn Leach	Y	Y	Y
Lynn Beasley	Y	Y	Y	Mark A. McClanahan	Y	Y	Y
David Belluck	Y	Y	N	John S. Morawetz	Y	Y	N
Robert Benson	Y	Y	Y	Deirdre L. Murphy	Absent	Absent	Absent
Kyle Blackman	Y	Y	N	Richard W. Niemeier	Absent	Absent	Absent
Jonathan Borak	Absent	Absent	Absent	William Pepelko	Y	Y	Y
William Bress	Y	Y	Y	Zarena Post	Absent	Absent	Absent
Luz Claudio	Y	Y	Y	George Rodgers	Y	Y	N
George Cushmac	Y	Y	Y	George Rusch, Chair	Y	Y	Y
Ernest Falke	Y	Y	Y	Michelle Schaper	Absent	Absent	Absent
Larry Gephart	Y	Y	Y	Bob Snyder	Y	Y	Y
John Hinz	Y	Y	N	Thomas Sobotka	Absent	Absent	Absent
Jim Holler	Y	Y	Y	Kenneth Still	Y	Y	Y
Thomas C. Hornshaw	Y	Y	Y	Patricia Ann Talcott	Absent	Absent	Absent
Nancy Kim	Absent	Absent	Absent	Richard Thomas	Y	Y	N
				Thomas Tuccinardi/ Doan Hansen	Absent Y	Absent Y	Absent N
				TALLY	26/26	26/26	18/26

PPM (mg/m ³)	30 Min	60 Min	4 Hr	8Hr
AEGL 1	N/A , ()	N/A , ()	N/A , ()	N/A , ()
AEGL 2	N/A , ()	N/A , ()	N/A , ()	N/A , ()
AEGL 3	1.5 , ()	1.1 , ()	0.54 , ()	0.38 , ()

* N/A = INSUFFICIENT DATA

AEGL 1 Motion: R. Hansen Second: R. Thomas

AEGL 2 Motion: R. Hansen Second: R. Thomas

AEGL 3 Motion: R. Benson Second: R. Snyder

Approved by Chair: [Signature] DFO: Paul S. Folin Date: 3/11/99

(509-14-8)

Date of NAC/AEGL Meeting: 3/11-12/99

Chemical:

TETRAINITROMETHANE

NAC Member	AEGL 1	AEGL 2	AEGL 3	NAC Member	AEGL 1	AEGL 2	AEGL3
George Alexeeff	N	N	Y	Loren Koller	Y	Y	Y
Steven Barbee	N	Y	Y	Glenn Leach	Y	Y	Y
Lynn Beasley	Y	Y	Y	Mark A. McClanahan	Y	Y	Y
David Belluck	N	Y	Y	John S. Morawetz	N	Y	Y
Robert Benson	Y	Y	Y	Deirdre L. Murphy	Absent	Absent	Absent
Kyle Blackman	Y	Y	Y	Richard W. Niemeier	Absent	Absent	Absent
Jonathan Borak	Absent	Absent	Absent	William Pepelko	Y	Y	Y
William Bress	Y	Y	Y	Zarena Post	Absent	Absent	Absent
Luz Claudio	Y	Y	Y	George Rodgers	Y	Y	Y
George Cushmac	Y	Y	Y	George Rusch, Chair	Y	Y	Y
Ernest Falke	Y	Y	Y	Michelle Schaper	Absent	Absent	Absent
Larry Gephart	Y	Y	Y	Bob Snyder	Y	Y	Y
John Hinz	Y	Y	Y	Thomas Sobotka	Absent	Absent	Absent
Jim Holler	Y	Y	Y	Kenneth Still	Y	Y	Y
Thomas C. Hornshaw	Y	Y	Y	Patricia Ann Talcott	Absent	Absent	Absent
Nancy Kim	Absent	Absent	Absent	Richard Thomas	Y	Y	Y
				Thomas Tuccinardi/ Doan Hansen	Absent	Absent	Absent
					Y	Y	Y
				TALLY	21/26	24/26	26/26

PPM, (mg/m ³)	30 Min	60 Min	4 Hr	8Hr
AEGL 1	0.69 ,()	0.49 ,()	0.24 ,()	0.17 ,()
AEGL 2	1.7 ,()	1.2 ,()	0.61 ,()	0.43 ,()
AEGL 3	3.5 ,()	2.4 ,()	1.2 ,()	0.87 ,()

AEGL 1 Motion: L. Koller Second: Bress Thomas

AEGL 2 Motion: L. Koller Second: Bress Thomas

AEGL 3 Motion: L. Koller Second: Bress Thomas

Approved by Chair: [Signature] DFO: Paul S. John Date: 3/11/99

624-83-9

Date of NAC/AEGL Meeting: 3/11-12/99

Chemical: METHYLISOCYANATE

NAC Member	AEGL 1	AEGL 2	AEGL 3	NAC Member	AEGL 1	AEGL 2	AEGL 3
George Alexeeff			Y	Loren Koller			Y
Steven Barbee			Y	Glenn Leach			Y
Lynn Beasley			Y	Mark A. McClanahan			A
David Belluck			Y	John S. Morawetz			Y
Robert Benson			Y	Deirdre L. Murphy	Absent	Absent	Absent
Kyle Blackman			Y	Richard W. Niemeier	Absent	Absent	Absent
Jonathan Borak			Y	William Pepelko			Y
William Bress			Y	Zarena Post	Absent	Absent	Y Absent
Luz Claudio			A	George Rodgers			Y
George Cushmac			Y	George Rusch, Chair			Y
Ernest Falke			Y	Michelle Schaper	Absent	Absent	Absent
Larry Gephart			Y	Bob Snyder			N
John Hinz			P	Thomas Sobotka	Absent	Absent	Absent
Jim Holler			Y	Kenneth Still			Y
Thomas C. Hornshaw			A	Patricia Ann Talcott	Absent	Absent	Absent
Nancy Kim	Absent	Absent	Absent	Richard Thomas			Y
				Thomas Tuccinardi/ Doan Hansen	Absent	Absent	Absent Y
				TALLY			22/23

PPM, (mg/m ³)	30 Min	60 Min	4 Hr	8Hr
AEGL 1	, ()	, ()	, ()	, ()
AEGL 2	, ()	, ()	, ()	, ()
AEGL 3	0.40 , ()	0.20 , ()	0.05 , ()	0.025 , ()

AEGL 1 Motion: _____ Second: _____

AEGL 2 Motion: _____ Second: _____

AEGL 3 Motion: R. Benson Second: E. Falke

Approved by Chair: [Signature] DFO: Paul S. Tobin Date: 3/12/99