



Threshold Limit Values for Chemical Substances (TLV[®]-CS) 2006

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This presentation will focus on the following:

- TLV[®] and *Documentation* revisions for 2006
- Particles Not Otherwise Specified (PNOS)
- Minimal Oxygen Content
- Inhalable Fraction and Vapor Endnote
- TLV[®] development process using Toluene Diisocyanate (TDI)





Revisions or Additions for 2006

- 677 TLV[®]-TWAs or TLV-Ceilings in the TLV[®]-CS section
- Under Study List
 - ✓ 104 substances
 - ✓ Group Guidance Values for Refined C₅ - C₁₅ Aliphatic and Aromatic Petroleum Hydrocarbons
 - ✓ Reciprocal Calculation Procedure
- 15 *Documentation* and associated TLVs[®] adopted in 2006
- 15 *Documentation* and associated TLVs[®] withdrawn due to insufficient data or replaced by new entries in 2006
- Notice of Intended Changes (NIC) for 2006
 - ✓ 3 new substances
 - ✓ 28 updated
 - ✓ Proposed withdraw of 1 *Documentation* and associated TLV[®]
 - ✓ Appendix F: Minimal Oxygen Content
 - ✓ Appendix G: Substances Whose *Documentation* and Adopted TLVs[®] Have Been Withdrawn



TLVs[®] Adopted in 2006

- Calcium sulfate
- Carbon disulfide
- Coumaphos
- Fenamiphos
- Fenthion
- Fonofos
- Iron oxide
- 2-Methoxyethanol
- 2-Methoxyethyl acetate
- Monochloroacetic acid
- Propylene
- Propylene dichloride
- Ronnel
- Silica, Crystalline
 - ✓ α -Quartz
 - ✓ Cristobalite
- 1,1,2,2-Tetrabromomethane



Documentation & Associated TLVs[®] withdrawn in 2006

Due to insufficient data

- Magnesite
- Perlite
- Silica, Amorphous - Diatomaceous earth (uncalcined)
- Silica, Amorphous
 - ✓ Precipitated silica
 - ✓ Silica gel
- Silica, Amorphous
 - ✓ Silica fume
- Silica, Amorphous
 - ✓ Silica fused
- Silica, Crystalline - Tripoli
- Silicon
- Tetrasodium pyrophosphate
- Vegetable oil mist

Replaced by New Entries with New TLVs[®]

- Acetylene tetrabromide
- Iron (Fe_2O_3) dust & fume, as Fe
- Rouge
- Silica, Crystalline - Cristobalite
- Silica, Crystalline - Quartz





2006 NOTICE OF INTENDED CHANGES (NIC)

| | |
|--|--|
| Alachlor | Methyl propyl ketone |
| Aldrin | α -Methyl styrene |
| Arsine | Mineral oil |
| Beryllium and compounds | 5-Nitro-o-toluidine |
| Carbaryl | Portland cement |
| Copper and inorganic compounds | N-Propanol |
| Diglycidyl ether [DGE] | Sulprofos |
| Dimethyl carbamoyl chloride | 1,1,1,2-Tetrachloro-2,2-difluoroethane |
| Dimethyl disulfide | 1,1,2,2-Tetrachloro-1,2-difluoroethane |
| 3,5-Dinitro-o-toluamide | Tetraethyl pyrophosphate [TEPP] |
| Ethyl amyl ketone | Thiram |
| Hexafluoropropylene | Toluene |
| Hydrogen sulfide | Toluene-2,4- or 2,6-diisocyanate |
| Hydroquinone | Trichloroethylene |
| Methyl demeton | Vanadium pentoxide |
| 1-Methyl naphthalene and 2-Methyl naphthalene | |



2006 NIC TLVs[®] to be Withdrawn

- Calcium carbonate – Insufficient data
- Copper, fume, dust, mist – Name change and new TLVs[®]
- Dinitolmide – Name change and new TLV[®]
- Oil mist, mineral – Name change and new TLV[®]



Appendix F: Minimal Oxygen Content 2006 NIC

- Sensitive tissues:
 - ✓ Brain and myocardium
- Initial symptoms:
 - ✓ Increased respiration and cardiac output
- Ensuing symptoms:
 - ✓ Headache
 - ✓ Impaired attention and thought processes
 - ✓ Decreased coordination
 - ✓ Impaired vision
 - ✓ Nausea
 - ✓ Unconsciousness, convulsions and death



Increased Respiration and Increased Cardiac Output Occur When the:

- Hemoglobin oxygen saturation is reduced below 90%.
- Partial pressure of oxygen (pO_2) in pulmonary capillaries drops below 60 torr.
- Corresponds to 120 torr pO_2 in the ambient air, due to anatomic dead space, CO_2 and H_2O vapor

Expressing Oxygen Requirements in Percent can be Problematic

- %O₂ does not change with altitude
- It is the ρO_2 in the lung that is important and therefore the ambient ρO_2 not the percent O₂
- ρO_2 of the atmosphere:
 - ✓ decreases with increasing altitude
 - ✓ decreases with the passage of low pressure weather events
 - ✓ decreases with increasing water vapor



19.5% O₂ Equivalent at Sea Level

- Corresponds to 148 torr ρO_2 , dry air
- Provides an adequate amount of oxygen for most work assignments
- Includes a margin of safety for altitudes less than @ 8000 ft
- Represents a concentration of 7.5% (75,000 ppm) of displacing gases
- Some displacing gases may have flammable properties or may produce physiological effects, so that their identity and source should be thoroughly investigated.





2006 ACGIH[®] Recommendation

- Oxygen deficiency: ambient $pO_2 < 132$ torr
- Recommends additional work practices when the ambient oxygen partial pressure is less than 132 torr
- Considers the use of 19.5% O_2 equivalent at sea level (148 torr) a useful guide that is protective against inert displacing gases and oxygen-consuming processes for altitudes up to 5000 feet and is protective for most weather conditions up to approximately 8000 feet





When the Ambient Oxygen Partial Pressure is Less than 132 torr, Additional Work Practices are Recommended:

- Thorough evaluation of confined spaces
- Use of continuous monitors integrated with warning devices
- Use workers acclimatized to altitude of work
- Use of rest-work cycles with reduced work rates and increased rest periods
- Training, observation and monitoring of workers
- Easy and rapid access to properly maintained oxygen supplying respirators



Nuisance Dust → PNOC → PNOS

- 1964: Nuisance dust introduced
15 mg/m³ or 50 mppcf, whichever less
- 1968: Nuisance Particulate Appendix added
- 1972: 10 mg/m³, total dust, or 30 mppcf
- 1976: 5 mg/m³, respirable added
- 1988: Appendix dropped, substances listed
- 1989: Changed to Particles Not Otherwise Classified (PNOC)
- 1995: 10 mg/m³, inhalable and 3 mg/m³, respirable (insoluble)
- 2001: Changed to Particles Not Otherwise Specified (PNOS)

Nuisance Dust Rationale

- Excessive concentrations may...
 - ✓ Seriously reduce visibility
 - ✓ Cause unpleasant deposits in eyes, ears, & nasal passages
 - ✓ Cause injury to the skin or mucous membranes by chemical or mechanical action or rigorous skin cleaning

(Also states that there is no particulate that does not provoke some response when inhaled in sufficient amounts)

Misuse of the “Inert” or “Nuisance Particulates” or “PNOC” TLV[®]

- Ignoring toxic constituents with TLVs
- Use for toxic materials which do not yet have a TLV[®]
- Inappropriate use on MSDSs
- Adoption by regulatory agencies

Appendix B: PNOS

- Do not have an applicable TLV[®]
- Insoluble or poorly soluble
- Low toxicity (i.e. not cytotoxic, genotoxic, or otherwise chemically reactive with lung tissue, not radioactive or a sensitizer, or toxic other than by inflammation or the mechanism of “lung overload”)
 - 3 mg/m³, respirable
 - 10 mg/m³, inhalable



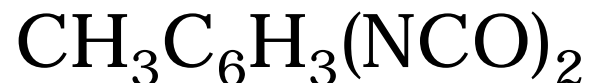
Inhalable Fraction and Vapor (IV Endnote)

- Material present in both particle and vapor phases
- Saturated Vapor Concentration (SVC)/TLV-TWA
- Also, consider both particle and vapor phases:
 - ✓ For spraying operations
 - ✓ For processes involving temperature changes
 - ✓ When a significant fraction of the vapor may be dissolved into or adsorbed onto particles of another substance (such as water-soluble compounds in high humidity environments)
 - ✓ In selecting sampling techniques to collect both states of matter

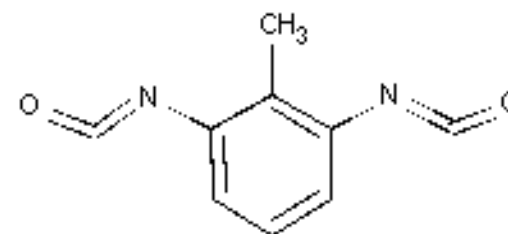
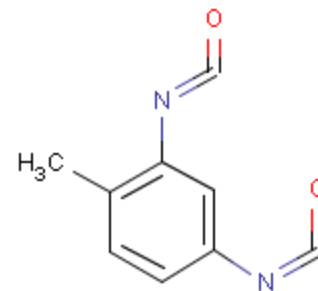




Toluene Diisocyanate (TDI)



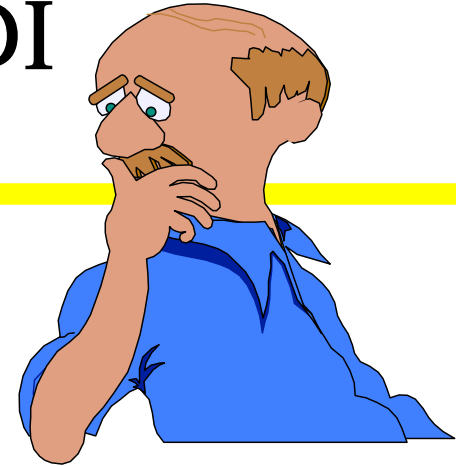
- 2,4- and 2,6-TDI (mixtures also)
- Generally liquid, but may be solid
- Volatile, with acrid odor
- Chemically reactive, heat and light-sensitive
- Used in polyurethane plastics, coatings, elastomers



| | |
|------------------|-----------|
| Current TLV-TWA | 0.005 ppm |
| Current TLV-STEL | 0.02 ppm |



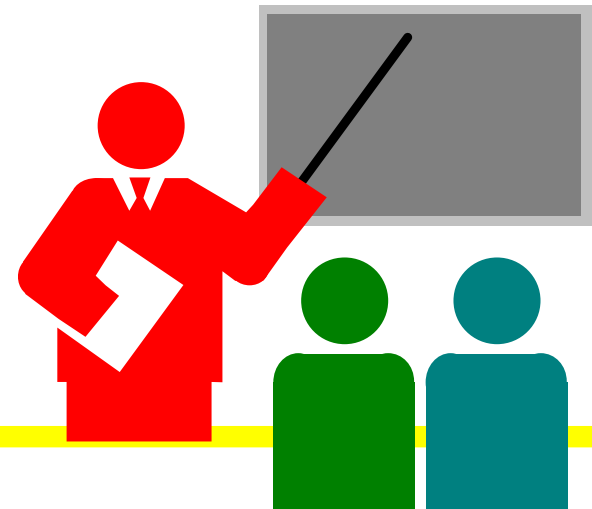
Some Important Issues in the Discussion of TDI



- Dose - response relationship for a sensitizer
- Evidence of sensitization
- Time-weighted average (TWA) *vs.* peak exposures
- Sensitized or susceptible individuals

ACGIH® TDI Symposium

- Held: April 22, 2002 (Cincinnati, OH)
- Presenters/Authors: Brown (and Burkert), Collins, Conner, Cummings (and Booth), Diller, Ott, Levine, Tarlo
- Published:
Appl. Occup. Environ. Hyg.
17(12): 838-908 (2002)





TDI Effect Levels

| | |
|-----------|--|
| 10 ppm | LC ₅₀ values |
| 1 ppm | Delayed death |
| 0.1 ppm | Inflammation, fibrosis, NOEL for reproductive effects |
| 0.05 ppm | Sensory irritation |
| 0.005 ppm | Cell adhesion, protein conjugation |
| 0.002 ppm | FEV ₁ reductions |
| ??? | OA |





Ott (2002): Table 1 TDI Production Units

| <u>Study</u> | <u>Period</u> | <u>% OA*</u> | <u>TDI (TWA, ppm)</u> |
|-------------------------|---------------|--------------|----------------------------|
| Adams, 1975 (N=565) | 1961-70 | 5.6 | decline % samples >0.02 |
| Porter, 1975 (N=300) | 1956-59 | 1.6 | 0.06 mean area |
| | 1960-69 | 0.8 | steady decline |
| | 1970-74 | 0.3 | <0.004 mean area |
| Weill, 1981 (N=277) | 1973-78 | 1.0 | 0.0016-0.0068** |
| Ott, 2000 (N=297) | 1967-79 | 1.8 | 0.0034-0.0101** |
| | 1980-96 | 0.7 | 0.0003-0.0027** |

* % OA (annual incidence)

** Range by job



Proposed TLV[®] for TDI

- TLV–TWA: 0.001 ppm (0.007 mg/m³), Inhalable fraction and vapor
- TLV–STEL: 0.003 ppm (0.021 mg/m³), Inhalable fraction and vapor
- Skin
- Sensitizer (SEN)
- A3 — Confirmed Animal Carcinogen with Unknown Relevance to Humans

TLVs[®]

- More than just “THE NUMBER”
- *TLV[®] Documentation:*
 - ✓ Critical health effects
 - ✓ NOAELs and LOAELs
 - ✓ Quality of the data relied upon and areas of uncertainty
 - ✓ Possible sensitive subgroups
 - ✓ Type of TLV[®] (TWA, STEL, C) and reason for selection
 - ✓ Notations
 - SKIN
 - SEN
 - Carcinogenicity