



Secretariat

Distr.
GENERAL

ST/SG/AC.10/C.4/2003/1
21 March 2003

Original: ENGLISH

**COMMITTEE OF EXPERTS ON THE TRANSPORT OF
DANGEROUS GOODS AND ON THE GLOBALLY
HARMONIZED SYSTEM OF CLASSIFICATION
AND LABELLING OF CHEMICALS**
Sub-Committee of Experts on the Globally
Harmonized System of Classification
and Labelling of Chemicals
(Fifth session, 7-9 July, 2003)

CLASSIFICATION OF GAS MIXTURES FOR TOXIC EFFECTS

Transmitted by the European Industrial Gases Association (EIGA)

Introduction

The document ST/SG/AC.10/C.4/2002/16/Add.3 allows under **3.1.3.6** a general Additivity formula to be used for mixtures. The above GHS document details principles to enable the classification of mixtures for acute toxic effects in respect of oral, dermal or inhalation toxicity. The paper allows the transition from pure products to mixtures and provides a formula that allows the calculation of the Acute Toxicity Estimate (ATE) when data are available for all ingredients. The following formula has been proposed:

The ATE of the mixture is determined by calculation from the ATE values for all relevant ingredients according to the following formula below for Oral, Dermal or Inhalation Toxicity:

$$\frac{100}{ATE_{mix}} = \sum_{i=1}^n \frac{C_i}{ATE_i}$$

where:

C_i = concentration of ingredient i
n ingredients and i is running from 1 to n
 ATE_i = Acute Toxicity Estimate of ingredient i.

This formula has been in use for many years in the transport regulations but is totally unfit for work place conditions. When applied to gases, the formula gives anomalous and a substantial understatement of the hazard. This leads to potentially dangerous results that could lead to personal injury or harm

To illustrate the dangers of adopting this method of calculation Table 1 below gives ATE values for three common gases; ammonia, carbon monoxide and hydrogen chloride when mixed with non toxic gases.(GHS Value %). For appreciation of the gross discrepancy, various accepted occupational exposure limits in **ppmV** have been added.

GE.03-

The following abbreviations are used:

- TWA: Time-Weighted Average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.
- STEL : Short term exposure limit is defined as a 15- minute TWA exposure which could not be exceeded at any time during a workday.
- IDLH: Immediately Dangerous to Life and Health, concentration from which a worker could escape without any escape-impairing symptoms or any irreversible health effects.

Table 1: Comparison between existing OEL values and GHS cut-off points

PRODUCT	VOLUME % IN MIXTURES	TOXICITY CATEGORY
AMMONIA TWA 25 ppmV STEL 35 ppmV IDLH 500 ppmV	Between 100 and 80% Between 80 and 40% Less than 40%	Category 3 Category 4 Non toxic
HYDROGEN CHLORIDE TWA 5 ppmV STEL 5 ppmV IDLH 100ppmV	Between 100 and 62.5% Between 62.5 and 31.2% Less than 31.2%	Category 3 Category 4 Non toxic
CARBON MONOXIDE TWA 25 ppmV STEL 400 ppmV IDLH 1500 ppmV	Between 100 and 75.2% Between 75.2 and 37.6% Less than 37.6%	Category 3 Category 4 Non toxic

It is quite obvious that a potential release of 376.000 ppmV of Carbon Monoxide, 250 times higher than the IDLH, cannot be considered as harmless. EIGA considers this approach unsafe and strongly recommends not adopting the formula for gases.

Proposal

EIGA proposes to retain the four categories as applicable to gases and base the categories on the approach adopted in the GHS for the other health hazards (Carcinogenic, mutagenic and reprotoxicity) and on the basis of modified EU (4 categories rather than 3), which has proved to work effectively and gives intuitively acceptable results.

Table 2. EIGA Proposal for cut-off points for gas mixtures

Gas classified	Concentration limits triggering classification of the mixture as			
	Category 1 *100 ppmV	Category 2 *500ppmV	Category 3 *2500ppmV	Category 4 *5000ppmV
Category 1	More than 1%	1.0-0.5%	0.5-0.2%	0.2-0.02%
Category 2		More than 2.0%	2.0-1.0%	1.0-0.2%
Category 3			More than 5%	5-0.5%
Category 4				More than 5%

* LC₅₀- 4 Hours.

For example under the existing GHS system the cut off point for a carbon monoxide mixture moving from the harmful to the toxic classification is 75.2 Vol % of CO whereas the cut off point in these EIGA proposals would be 5 Vol %. If these concentrations are compared with the IDLH (Immediately dangerous to life or health value) of 1500 ppmV (0.15 Vol %) and the STEL (Short term exposure level) of 400 ppmV (0.04 Vol %) it is apparent that the method of calculation in the EIGA proposal is more applicable and safer than the existing ATE formula.
