Limitations on GHS Applicability to Section 14 of the SDS

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Welcome to this SCHC Annual Meeting presentation:

GHS vs. Dangerous Goods:
Section 14 Might Be More Difficult Than You Realize!

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Distilling SDS info into transport classifications

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What's NOT addressed

- pH
- Living organisms
- Articles

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ARTICLES

- Regulated for transport
  - Engines and Vehicles
  - Fuel Cells, Batteries, and Capacitors
  - Air Bags
  - Seat Belt Pretensioners
  - Shock Absorbers and Struts
  - Thermometers
  - Life-Saving Appliances

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Air Carriers check classifications via mSDS







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So, now, are more ground carriers



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Consequences of mSDS TDG mismatch?

- Shipment rejection or delay
- Hassle
- Time wasted
- Unhappy customers
- Referrals to enforcement?
- Two ways to communicate one hazard
- Eventual user ennui
- Defeating the purpose of safety regulations

8

GHS definitions versus TDG definitions

- We already know of disharmonization @ UN
  - Eye corrosion
  - pH, maybe?
  - 4 hour toxicity or 1 hour toxicity
- Well known issues aren't today's emphasis

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What is the pictogram for these liquids?

- Fictionalium -- inhl rat LC50 1,001 mL/m3/1H
- Genatropium -- inhl rat LC50 1,001 mL/m3/1H
- Eugenium -- inhl rat LC50 1,001 mL/m3/1H

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TABLE A.1.1—ACUTE TOXICITY HAZARD CATEGORIES AND ACUTE TOXICITY ESTIMATE (ATE) VALUES DEFINING THE RESPECTIVE CATEGORIES

Exposure route	Category 1	Category 2	Category 3	Category 4
Oral (mg/kg bodyweight) see: Note (a), Note (b)	≤5	>5 and ≤50	>50 and ≤300	>300 and ≤2000.
Dermal (mg/kg bodyweight) see: Note (a), Note (b)	≤5	>50 and ≤200	>200 and ≤1000	>1000 and ≤2000.
Inhalation—Gases (ppmV) see: Note (a), Note (b), Note (c)	≤100	>100 and ≤500	>500 and ≤2500	>2500 and ≤20000.
Inhalation—Vapors (mg/l) see: Note (a), Note (b), Note (c), Note (d).	≤0.5	>0.5 and ≤2.0	>2.0 and ≤10.0	>10.0 and ≤20.0.
Inhalation—Dusts and Mists (mg/l) see: Note (a), Note (b), Note (c)	≤0.05	>0.05 and ≤0.5	>0.5 and ≤1.0	>1.0 and ≤5.0.

Note: Gas concentrations are expressed in parts per million per volume (ppmV).
Notes to Table A.1.1:
(a) The acute toxicity estimate (ATE) for the classification of a substance is derived using the LD_{50}/LC_{50} Stewardwhere available;
(b) The acute toxicity estimate (ATE) for the classification of a substance or ingredient in a mixture is derived using:
(i) the LD_{50}/LC_{50} where available. Otherwise,
(ii) the appropriate conversion value from Table 1.2 that relates to the results of a range test, or
(iii) the appropriate conversion value from Table 1.2 that relates to a classification category;
(c) Inhalation cut-off values in the table are based on 4 hour testing exposures. Conversion of existing inhalation toxicity data which has been generated according to 1 hour exposure is achieved by dividing by a factor of 2 for gases and vapors and 4 for dusts and mists;

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What is the pictogram for these liquids?

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- Eugenium -- inhl rat LC50 1,001 mL/m3/1H



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What is the Section 14 for these liquids?

- Fictionalium -- inhl rat LC50 1,001 mL/m3/1H
  - Vapor Pressure @ 20C = 300 mmHg
- Genatropium -- inhl rat LC50 1,001 mL/m3/1H
  - Vapor Pressure @ 20C = 7.32 mmHg
- Eugenium -- inhl rat LC50 1,001 mL/m3/1H
  - Vapor Pressure @ 20C = 0.00314 mmHg

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$$V = (VP/atm) \times 10^6$$

(2)(i) The packing group and hazard zone assignments for liquids (see §173.115(c) of this subpart for gases) based on inhalation of vapors shall be in accordance with the following table:

Packing Group	Vapor concentration and toxicity
I (Hazard Zone A)	V ≥500 LC_{50} and LC_{50} ≤200 mL/M3.
I (Hazard Zone B)	V ≥10 LC_{50}; LC_{50} ≤1000 mL/m3; and the criteria for Packing Group I, Hazard Zone A are not met.
II	V ≥LC_{50}; LC_{50} ≤3000 mL/m3; and the criteria for Packing Group I, are not met.
III	V ≥.2 LC_{50}; LC_{50} ≤5000 mL/m3; and the criteria for Packing Groups I and II, are not met.

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What is the Section 14 for these materials?

- Fictionalium -- inhl rat LC50 1,001 mL/m3/1H
  - Vapor Pressure @ 20C = 300 mmHg
    - 6.1, I, Hazard Zone B



- Genatropium -- inhl rat LC50 1,001 mL/m3/1H
  - Vapor Pressure @ 20C = 7.32 mmHg
    - 6.1, II



- Eugenium -- inhl rat LC50 1,001 mL/m3/1H
  - Vapor Pressure @ 20C = 0.00314 mmHg
    - Not DG



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SDS criteria versus Transport Criteria, round 1

Does this:



+ "liquid",

always mean this?



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2.2. Label elements

GHS-US labeling

Hazard pictograms (GHS-US) :



Signal word (GHS-US) : Danger

Hazard statements (GHS-US) : H220 - EXTREMELY FLAMMABLE GAS
H280 - CONTAINS GAS UNDER PRESSURE; MAY EXPLODE IF HEATED
OSHA-H01 - MAY DISPLACE OXYGEN AND CAUSE RAPID SUFFOCATION.
CGA-HG04 - MAY FORM EXPLOSIVE MIXTURES WITH AIR
CGA-HG08 - BURNS WITH INVISIBLE FLAME.



(b) Division 2.2 (*non-flammable, nonpoisonous compressed gas—including compressed gas, liquefied gas, pressurized cryogenic gas, compressed gas in solution, asphyxiant gas and oxidizing gas*). For the purpose of this subchapter, a non-flammable, nonpoisonous compressed gas (Division 2.2) means any material (or mixture) which—

(1) Exerts in the packaging a gauge pressure of 200 kPa (29.0 psig/43.8 psia) or greater at 20 °C (68 °F), is a liquefied gas or is a cryogenic liquid, and

(2) Does not meet the definition of Division 2.1 or 2.3.

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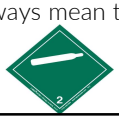
SDS criteria versus Transport Criteria, round 2

Does this:



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always mean this?



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SDS criteria versus Transport Criteria, round 3

Does this:

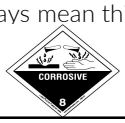




,



always mean this?



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Have you met Willy Pete?

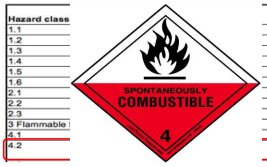
- White Phosphorus



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Pyrophoric Solid





Hazard class
1.1
1.2
1.3
1.4
1.5
1.6
2.1
2.2
2.3
3 Flammable
4.1
4.2

Label name
EXPLOSIVES 1.1
EXPLOSIVES 1.2
EXPLOSIVES 1.3
EXPLOSIVES 1.4
EXPLOSIVES 1.5
EXPLOSIVES 1.6
FLAMMABLE GAS
NONFLAMMABLE GAS
POISON GAS
FLAMMABLE LIQUID (none)
FLAMMABLE SOLID
SPONTANEOUSLY COMBUSTIBLE

Phosphorus, white dry or Phosphorus, white, under water or Phosphorus white, in solution or Phosphorus, yellow dry or Phosphorus, yellow, under water or Phosphorus, yellow, in solution	4.2	UN1381	I	4.2 0.1	B9, B26, N34, T9, TP3, TP31	None	188	243	Forbidden	Forbidden	E

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SDS criteria versus Transport Criteria, round 4

Does this:



+ “solid”,

always mean this?

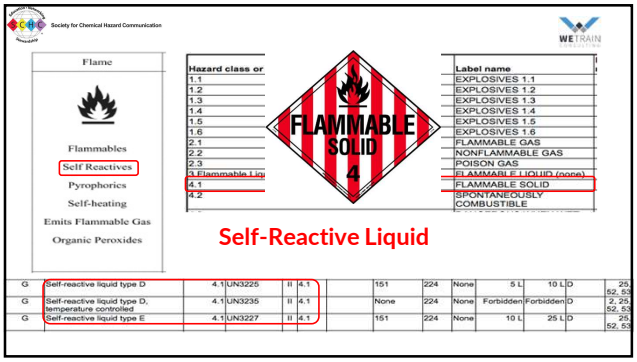


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Get Up & Go?

- Your brand new fuel additive product bears a red & white, stripey DG/HazMat label with the words “Flammable Solid” on it. Yet, the mSDS has a bomb pictogram and says your product is a liquid. The same person who does your transportation classifications writes your mSDSs.
- Do you fire her?
- Why not? How could she be right?

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SDS criteria versus Transport Criteria, round 5

Does this:



+ "liquid",

always mean this?



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Benzoyl Peroxide = Dibenzoyl Peroxide



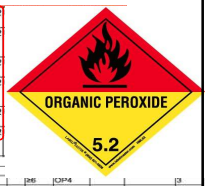
Exploding Bomb

Explosives

Self Reactives

Organic Peroxides

G	Organic peroxide type B, solid, temperature controlled		5.2						
G	Organic peroxide type C, liquid		5.2						
G	Organic peroxide type C, liquid, temperature controlled		5.2						
G	Organic peroxide type C, solid		5.2						
G	Organic peroxide type C, solid, temperature controlled		5.2						
G	Organic peroxide type D, liquid		5.2						



Dibenzoyl peroxide	UN3102	>51-100				≥6	IP4		3
Dibenzoyl peroxide	UN3102	>77-94							
Dibenzoyl peroxide	UN3104	≤77				≥23	OP6		
Dibenzoyl peroxide	UN3106	≤62			≥28	≥10	OP7		
Dibenzoyl peroxide [as a paste]	UN3106	>52-62					OP7		21
Dibenzoyl peroxide	UN3106	>35-52			≥48		OP7		
Dibenzoyl peroxide	UN3107	>36-42		≥18		≤40	OP8		
Dibenzoyl peroxide [as a paste]	UN3108	≤56.5				≥15	OP8		
Dibenzoyl peroxide [as a paste]	UN3108	≤52					OP8		21
Dibenzoyl peroxide [as a stable dispersion in water]	UN3109	≤42					OP8		
Dibenzoyl peroxide	Exempt	≤35				≥65	Exempt		29

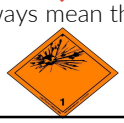
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SDS criteria versus Transport Criteria, round 6

Does this:



always mean this?



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What shall we name these new peppers?

- Using old-fashioned pollination control techniques, but *not* any molecular biology techniques, your botanists have created a new type of very flavorful, ultra-hot pepper plant. It is not a GMO.
- Extracts from the new peppers are dried and milled. The extract is not corrosive, not toxic per animal data, and not a readily combustible solid per burning rate tests. But it is very irritating, to both skin and eyes, especially in high concentrations at close range. Your mSDS gives it the Exclamation Point pictogram.

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Eat it? Or spray it?

Exclamation Mark

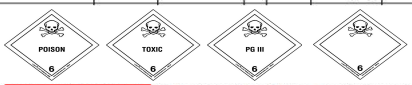


Irritant

	Tear gas candles			6.1	UN1700	6.1, 4.1
	Tear gas cartridges, see Ammunition, tear-producing, etc.					
D	Tear gas devices with more than 2 percent tear gas substances, by mass	6.1	NA1693	I	6.1	
				II	6.1	
	Tear gas devices, with not more than 2 percent tear gas substances, by mass, see Aerosols, etc					
	Tear gas grenades, see Tear gas candles					
G	Tear gas substance, solid, n.o.s.	6.1	UN3448	I 6.1 II 6.1	T6, TP33 IB8, IP2, IP4, T3, TP33	None None

Narcotic Effects

Respiratory Tract Irritation



(2) Is an irritating material, with properties similar to tear gas, which causes extreme irritation, especially in confined spaces.

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SDS criteria versus Transport Criteria, round 7

Does this:



,

always mean this?



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Help me drop my M, please *(MSDS → SDS)*

SECTION 2 HAZARDS IDENTIFICATION

CLASSIFICATION: Xn; R20 | Xn; R65 | R66

IMMEDIATE HEALTH EFFECTS

Eye: Not expected to cause prolonged or significant eye irritation.

Skin: Skin contact may cause drying or defatting of the skin. Symptoms may include pain, itching, discoloration, swelling, and blistering

Ingestion: Because of its low viscosity, this material can directly enter the lungs, if swallowed, or if subsequently vomited. Once in the lungs it is very difficult to remove and can cause severe injury or death.

Inhalation: May be harmful if inhaled.

DELAYED OR OTHER HEALTH EFFECTS: Not classified.

ENVIRONMENTAL EFFECTS: Not classified.

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Aspiration Hazard

Health Hazard

Carcinogen
Respiratory Sensitizer
Reproductive Toxicity
Target Organ Toxicity
Mutagenicity
Aspiration Toxicity



§173.132 Class 6, Division 6.1—Definitions.

(a) For the purpose of this subchapter, *poisonous material* (Division 6.1) means a material, other than a gas, which is known to be so toxic to humans as to afford a hazard to health during transportation, or which, in the absence of adequate data on human toxicity:

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SDS criteria versus Transport Criteria, round 8

Does this:



,

always mean this?



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Class 3, the easiest class?

Packing group	Flash point (closed cup)	Initial boiling point
I	--	≤ 35°C
II [a]	< 23°C	> 35°C
III [a]	≥ 23°C ≤ 60°C	> 35°C

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GHS vs. DG

- Flash Point 24°C, Boiling Point 34°C
  - DG → PG I
  - GHS?

How are flammable liquids classified under OSHA's HCS?

Table 1 shows the classification criteria and label elements:

Table 1: Classification Criteria and Label Elements

Category	Category 1	Category 2	Category 3	Category 4
Description	Flash point < 23°C (73.4°F) and initial boiling point ≤ 35°C (95°F)	Flash point < 23°C (73.4°F) and initial boiling point > 35°C (95°F)	Flash point ≥ 23°C (73.4°F) and ≤ 60°C (140°F)	Flash point > 60°C (140°F) and ≤ 93°C (199.4°F)
Pictogram				*No symbol*
Signal Word	Danger	Danger	Warning	Warning
Hazard Statement	Extremely flammable liquid and vapor	Highly flammable liquid and vapor	Flammable liquid and vapor	Combustible liquid

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GHS vs. DG

Does GHS flammable liquid category 3 ALWAYS equate to 3, III?

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Other Class 3 classification variances

- Change of PG, based upon viscosity
  - ...and size of package,
  - ...and mode shipped.
    What do we put in Section 14 for these?
- Sustaining Combustion, or not

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Size Matters!

GENE-O-SOL 5 gallon
88% water
1% soap
10% chloroform
1% fragrance & color

Not HazMat (DG)

GENE-O-SOL 55 gallon
88% water
1% soap
10% chloroform
1% fragrance & color

RQ (Chloroform) => DG

2-Chloroethyl vinyl ether	1000 (454)
Chloroform	10 (4.54)
Chloromethane	100 (45.4)

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Size Matters!

- ID8000 << UNxxxx
  - Inner: 120 mL, 500 mL, 820 mL, 500 g. Outer: 30 kgG
- 4.2 Self-heating
  - 450 L or 3 m^3
- U.S. Combustible Liquids
  - 450 L

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Just because we said so...

+Methanol

+ I	Methanol	3	UN1230	II	3, 6.1	IB2, T7, TP2	150	202	242	1 L	60 L	B	40
D	Methanol	3	UN1230	II	3	IB2, T7, TP2	150	202	242	1 L	60 L	B	40

+ I	Methanol	3	UN1230	II	3, 6.1
D	Methanol	3	UN1230	II	3

§173.132 Class 6, Division 6.1—Definitions.

(a) For the purpose of this subchapter, *poisonous material* (Division 6.1) means a material, other than a gas, which is known to be so toxic to humans as to afford a hazard to health during transportation, or which, in the absence of adequate data on human toxicity:

(1) Is presumed to be toxic to humans because it falls within any one of the following categories when tested on laboratory animals (whenever possible, animal test data that has been reported in the chemical literature should be used):

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Intended Use

- ID8000 & Expired ORM-D
  - Consumer Commodity, 9
- Medicines (Pharmaceuticals, Drugs)
  - No equivalent to ADR SP 601 in other DG regulations
    - Not a mode, but an origin/destination consideration, as well as a usage issue.

Hazardous material means a substance or material that the Secretary of Transportation has determined is capable of posing an unreasonable risk to health, safety, and property when transported in commerce, and has designated as hazardous under section 5103 of Federal hazardous materials transportation law (49 U.S.C. 5103). The term includes hazardous substances, hazardous wastes, marine pollutants, elevated temperature materials, materials designated as hazardous in the Hazardous Materials Table (see 49 CFR 172.101), and materials that meet the defining criteria for hazard classes and divisions in part 173 of this subchapter.

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Destinations (and origins and stops)

- IATA State (country, nation) variations
  - esp. if forbidden somewhere
- USDWW, TWW, SWICWWRTG
  - + water → ↑2.3
- ADR SP 601 (medicines)

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Packaging



UN1950, Aerosols versus UN*xxxx*, Refrigerant Gas

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Wave your arms around, please.

- Is air dangerous?



UN1002

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PACKAGING

- Chemical kits
- First aid kits

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Conditions of Transport -- Temperature

- UN1845, Dry Ice, 9
- UN2187, Carbon Dioxide, Refrigerated Liquid, 2.2
- UN3256, Elevated Temperature Liquid..., 3
- UN3257, Elevated Temperature Liquid..., 9
- UN3258, Elevated Temperature Solid..., 9

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FORM

- Sulphur (sulfur)
  - Non-reg when pressed into a solid shape
  - Also a size consideration applies to the powder
- Calcium hypochlorite, dry
  - If non-friable tablet, then PG II → PG III

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Maybe non-GHS, but perhaps DG regulated

- Aviation Regulated
  - Anaesthetic properties, or stench, or irritating…
    - Another SUBJECTIVE decision
- Elevated Temperature
  - Can take a material from non-DG to DG
    - Class 9 or Class 3, depending…
- Polymerizing Materials
  - Although GHS may adopt this in the future

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LISTS matter

- RQ / Hazardous Substance
  - …and size, too.
- US Marine Pollutants
  - Not just the list, but…
    - …mode and
    - …size, too.

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BONUS EXAMPLE:

- Your seafood supply company ships live crabs (*not the microorganisms, but the macroorganisms*) all over the globe, next day air. Each full moon, plus & minus 2 days, one type of crab secretes large quantities of pheromones that rapidly corrode aluminum. When your carriers and customers demand mSDSs, what will you put in Section 14, and why?

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WHAT DID WE LEARN?

What are ALL the factors that affect mSDS Section 14?

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FACTORS AFFECTING SECTION 14 ENTRY

GHS criteria
DG criteria

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Distilling SDS info into transport classifications

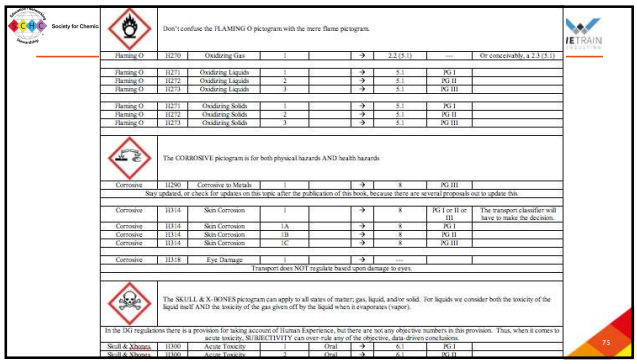
Notwithstanding subjectivity, it'd be nice to take SDS/product warnings and directly apply them to transport classifications.
In particular, it would be helpful if the existence of a pictogram proved the necessity of a transport label & placard. Let's see if this practice would be supported, by examining some pictograms and some potentially corresponding transport labels.

Pictogram		Label	Discussion	Correspondence?
			The exploding bomb pictogram can apply to 4.1 self-reactives or 5.2 organic peroxides, as well as to Class 1	SOMETIMES
			The compressed gas pictogram applies to 2.1 flammable gases and 2.3 toxic gases, as well as to Division 2.2	SOMETIMES
GAS			Beware of the 4 hr ▯ ▯ 1 hr conversions, but each time the flame pictogram is required for a gas, it's 2.1	ALWAYS
LIQUID			The flame pictogram for a liquid could be for a 4.2 pyrophoric liquid or a 4.1 self-reactive, as well as to Class 3	SOMETIMES
SOLID			The flame pictogram for a solid could be for a 4.2 pyrophoric solid or a 4.1 self-reactive, as well as to Division 4.1	SOMETIMES
			Each time the flaming O pictogram is required, the material is 5.1	ALWAYS
GAS			Beware the 4 hr ▯ ▯ [illegible] skull & bones pictogram is required for a gas, it's 2.3	ALWAYS
LIQUID			Volatility is not required when calculating vapor toxicity for the skull & bones pictogram, but is for 6.1 liquids	SOMETIMES
SOLID			Each time the skull & bones pictogram is required for a solid, it's 6.1	ALWAYS
			The corrosive pictogram could be solely for eye corrosion, something transport doesn't regulate as Class 8.	SOMETIMES
			The exploding chest pictogram could be for an aspiration hazard which can also be Division 6.1 by inhalation.	SOMETIMES
			The exclamation point pictogram could be for a severe irritant of Div. 6.1 or for an aviation regulated Class 9.	SOMETIMES

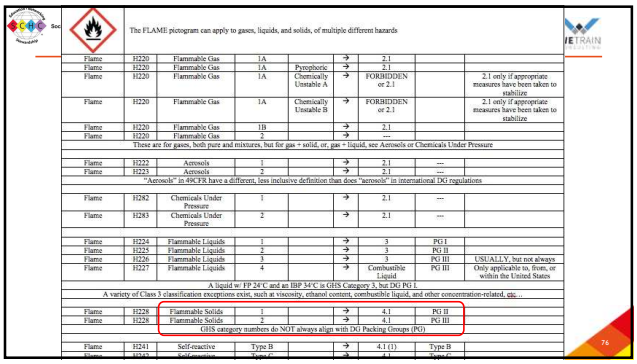
Gene Sanders, CDGT, DGSA
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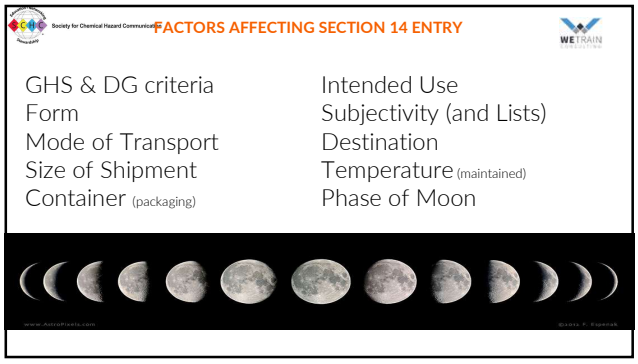
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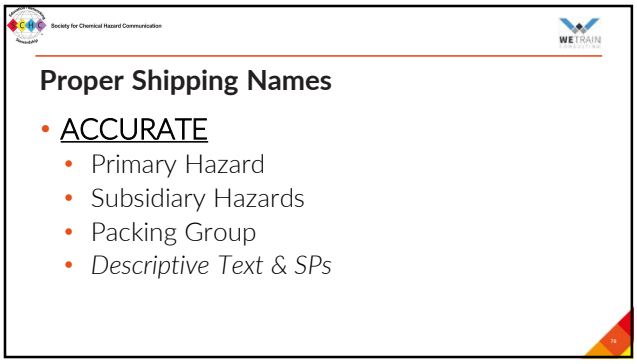
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Proper Shipping Name Modification

- Waste
- Mixture or Solution
- HOT
- Stabilized
- Molten
- Sample
- Add-ons
  - Technical Name
  - RQ
  - MP

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When Section 14 doesn't match the rest of the SDS…

- …because of an 'oddity' in the reg's…
- …would a legal disclaimer help?
- John Mayfield's interpretation of a disclaimer:
- "This classification's no damn good"

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There's even more we didn't cover, though…





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PRE-TRAINING IS REQUIRED

- Everyone who completes Section 14 for a DG is required to have DG (Dangerous Goods, HazMat for transport) classification training.
  - 49CFR: 172.702(b), 172.704(a)(2)(i)
  - IATA: 1.5.0.2, 1.5.0.4, Table 1.5.A
  - IMDG: 1.3.1.1, 1.3.1.2 *(esp. 1.3.1.2.2)*
  - ADR: 1.3.2.2, 1.4.2.1.1(a)
  - TDG: 6.1(1)(a), 6.2(a)-(c)

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THANK YOU

- Any more questions?

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