

*Review of Hydrogen Peroxide  
Specification MIL-P-16005E*

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7/9/01

# *Overview*

- History of US Hydrogen Peroxide Specifications
- Specification Sections
  - Scope
  - Applicable Documents
  - Requirements
  - Quality Assurance
  - Preparation for Delivery
  - Notes
- Need for New Specification
- Recommendations
- Present Work
- Conclusions

# *History of US H2O2 Mil Specifications*

- MIL-P-16005 (90% & 98%)
  - Rev E Released Jan, 1968 Canceled Jun, 1988
  - Intended to Control Rocket Oxidizer, Mono-propellant
  - Use in programs: Redstone, X-15, etc..
  - Cancellation Coincident with Scout Vehicle Termination
  - Peroxide made by three different methods:electrolytic, AO & Alcohol
- MIL-H-22868 (70% & 90%)
  - March, 1961 Rev Canceled July, 1996
  - Intended in Use for Torpedoes
  - Much Greater Stabilizer Levels than MIL-P-16005

# Scope

- MIL-P-16005E
  - Type I - 91% max, 90% min (by weight)
  - Type II - 99% max, 98% min (by weight)
- Today Without Government Specification
  - 85% Air Liquide, discontinued production
  - 85% SI, discontinued production
  - 87.5%, 89.5% Degussa, discontinued production
  - 90%, 98% Degussa
  - 90%, 98% FMC
  - ~80 to 98% Various Home Brews

# *Applicable Documents*

- MIL-P-16005E
  - 49 CFR 171-190 (DOT Haz Matl Regs)
  - ASTM standards, Parts 8, 17, 30 (Matl Test)
- Today without Government Specification
  - 49 CFR 171-190
  - Propellant Producer Testing Stds

# Requirements

- MIL-P-16005E (same for 98%)

	MIL-P-16005	Du Pont	Shell	FMC
Percent H <sub>2</sub> O <sub>2</sub>	90 to 91	90.7	90.7	90.8
Percent AOL	2.0 max.	0.9	0.3	1.1
Carbon, mg/l	200 max.	11	150	0
Residue, mg/l	20 max.	15	15	15
Chloride, mg/l	1.0 max.	0.2	< 0.1	0.2
Phosphate, mg/l	0.2 max.	0.1	0.04	0.07
Nitrate, mg/l	3.0 to 5.0	3	3.6	3.5
Sulfate, mg/l	3.0 max.	0.3	< 3.0	0.02
Tin, mg/l	1.4 to 4.0	1.8	1.8	1.9
Ammonium, mg/l	3.0 max.	0.3	< 3.0	0.03
Aluminum, mg/l	0.5 max.	0.2	0.2	0.07
Particulate, mg/l	1.0 max.	< 1.0	< 1.0	< 1.0

## *Requirements (Cont.)*

- Today Without Government Specification
  - 90% Degussa, some stabilizer levels > 16005E
  - 90% FMC, does meet 16005E but different than historical fluid
  - 98% Degussa, FMC booth meet or close to meeting 16005E
  - ~98% Various Home Brew governed, does/doesn't meet 16005E
  - All Fluid Produced by AO process
  - Electrolytic nor Alcohol Processes No Longer used
  - Relevance of Historical Data on Catalyst Unknown but Different

# *Quality Assurance*

- MIL-P-16005E
  - Defines sampling methods
  - Defines methods for determination of impurity levels
  - Defines how to make test solutions
  - Titration methods
  - The bulk of the specification; 22 pg of 27 pgs total
- Today without Government Specification
  - Producer preferred methods
  - Newer test methods
    - ICP-MS (inductive coupled plasma-mass spec) for Metals
    - IC (ion chromatography) for Ions



# *Preparation for Delivery*

- MIL-P-16005E
  - Containers conform to 49 CFR 171-190
  - Drums also must also conform to:
    - made of DOT 42D approved aluminum
    - less than 55 gal with vented closure in top head
  - Cargo tanks and tank cars must also conform to:
    - Aluminum (1060, 1260, 5254, 5652)
    - Venting and pressure relief as defined by Bureau of Explosives
- Today without Government Specification
  - Propellant Producer Conformance to 49 CFR171-190
  - Some Conform to MIL-P-16005, Some Don't

# *Hazards Matl Table 49CFR172.101*

*(Delivery, con.t)*

- Haz matl Description and Proper shipping names:
  - Hydrogen peroxide, stabilized or hydrogen peroxide aqueous solutions, stabilized with more than 60% hydrogen peroxide
- Hazard Class or Division: 5.1
- Identification Numbers: UN2015
- Packaging Group: I
- Label Codes: 5.1, 8
- Special Provisions: 12, A3, A6, **B53**, B80, B81, B85, T15, T37
- Packaging Section:
  - Exceptions: None
  - **Non-Bulk: 49CFR173.201**
  - Bulk: 49CFR173.243
- Qnty Limits:
  - Passenger Aircraft/rail: Forbidden
  - Cargo Aircraft: Forbidden
- Vessel Storage:
  - Location: D

# *Hazard Class and packing Group*

## *49CFR173.127*

*(Delivery Cont.)*

- Liquid material classified as Division 5.1:
  - If when tested according to UN Manual of Test & Criteria:  
Spontaneously ignites or its mean time for pressure rise from 690 kPa to 2070 kPa gauge is less than the time of a 1:1 Nitric acid (65%)/Cellulose mixture.
- Packaging group I: Any material which spontaneously ignites when mixed with cellulose in a 1:1 ratio

# *Applicable Special Provisions*

## *49CFR172.102*

### *(Delivery Cont.)*

- 12: In concentrations greater than 40%, this material has strong oxidizer properties and is capable of starting fires in contact with combustible material. If appropriate, a package containing this material must conform to additional labeling req. of section 172.402.
- A3: For combination packaging, if glass inner packaging (including ampoules) are used, they must be packed with absorbent material in tightly closed metal receptacles before packing in outer packings.
- A6: For combination packaging, if plastic inner packaging are used, they must be packed in tightly closed metal receptacles before packing in outer packings.
- ***B53: Except for IBCs, packaging must be made of either Al or Steel.***
- B80: Each Cargo tank must have a min design pressure of 276 kPa (40 psig)
- B81: Venting and Pressure relief devices for tank car tanks and cargo tanks must be approved by the Associate Administrator for Hazardous Material Safety
- B85: Cargo tanks must be marked with the name of the lading in accordance with requirements of Section 172.302(b)

# *Packaging (Delivery Cont.)*

- Bulk: See 49CFR173.243 (Acceptable Railcar and Cargo tank DOT Specs)
- ***Non-Bulk: See 49CFR173.201***
  - ***Outer packings:***
    - *Steel Drums: 1A1 or 1A2*
    - *Al Drums: 1B1 or 1B2*
    - *Others: Not permitted per special provisions*
  - ***Inner Packings:***
    - *Glass, Plastic Receptacles, Metal receptacles, glass ampoules*
  - ***Single Packings:***
    - *Steel Drums: 1A1 or 1A2*
    - *Al Drums: 1B1 or 1B2*
    - *Others: Not permitted per special provisions*

# *Vessel Storage (Delivery Con.t)*

- Location (49CFR101):
  - D: Must be stored “on deck only” on a cargo vessel and on a passenger vessel carrying a number of passengers limited to not more than the larger of 25 passengers or one passenger per each three meters of overall vessel length, but material is prohibited on passenger vessels in which the limiting number of passengers is exceeded.
- Other (49CFR84):
  - 25: Shade from radiant heat
  - 66: Stow “separated from” flammable solids
  - 75: Stow “separated from” permanganates
  - 106: Stow “separated from” powdered metals

# *Non-Bulk - Drums Standards*

## *(Delivery Cont.)*

- ***Steel Drums (49CFR178.504)***

- *1A1: Non-removable Head, 1A2: Removable Head*
- *Rolling hoops required for > 16 gal*
- *max 119 gal or 882 lbm*
- *Dimensions for filling, empty and vent bodies in heads*
- *49CFR178.504 (7)*
  - *If material used for body, heads, closures and fittings are not themselves compatible with contents to be transported, suitable internal protective coatings or treatments must be applied. These coatings or treatments must retain their protective properties under normal conditions of transport.*

- ***Al Drums (49CFR178.505)***

- *1B1: Non-removable Head, 1B2: Removable Head*
- *Rolling hoops required for > 16 gal*
- *max 119 gal or 882 lbm*
- *Dim for filling, empty and vent bodies in heads*
- *No comments on liners*

# *Drums - General (Delivery Cont.)*

- Testing of packaging: See 49CFR178.601
  - Drop test: 49CFR178.603
  - leak-proof: CFR178.604
  - hydrostatic pressure: CFR178.605
  - stacking: CFR178.606
  - cooperage: CFR178.607
- UN Designation/markings
  - Example for HP use: UN1B1-X1.5-250
    - 1B1: UN Designation for AL Non-Removable Head
    - X: level of risk (X, Y or Z) where X requires 6 ft drop
    - 1.5: Specific gravity of fluid which may be carried
    - 250: leak tested pressure in kPa
- Labels/Placards (49CFR172.550)



# *Problems with CFR Only Conformance*

## *(Delivery, Cont.)*

- CFR Requirements permit drums that are higher risk for rocket grade HP
  - Non Class 1 tank: example - carbon steel with removable head & bag polyethylene liner
    - Bag failure provides direct contact of fluid with class 4 material
      - Which provides enough local energy to combust with polyethylene liner.
      - May produce internal over pressurization and drum failure
    - Drop on head clamp may result in failure and spillage of HP to environment which may result in fire external to drum.
  - Several vendors have used drums which conform to CFR but may cause hazardous conditions
    - Unlined Stainless Steel Drum, Non-removable head
    - Polymeric Bag lined Carbon Steel Drum, Removable head
- Other Transportation problems
  - Palletization (Should not be shipped with wood or any other combustible material)
  - Secondary Confinement Desirable
  - Prevention from inversion where the venting device may be filled by HP

# *Recommended Drum*

*(Delivery Cont.)*



# *Notes*

- MIL-P-16005E
  - Intended use as oxidizer for mono-propellant rockets
  - Ordering data (test reports required)
  - Specification Analysis Sheet sample (DD form)
- Today without Government Specification
  - Inconsistent Procurement Data Practices

# *Need for New Specification*

- Standard Specification Missing from present day work
  - Each end user has their own (or lack thereof)
  - Each Producer has their own
- Peroxide Community Has NO Common Reference
  - Confusion About Effect of Stabilizer, Impurity Levels
  - Direct Data Comparison Between Users Products is Difficult
  - Present Test Data Will Have Unnecessary Dispersions
  - Potentially Unsafe Transportation/Handling (Black Eye for H<sub>2</sub>O<sub>2</sub>)
  - Stabilizer/Impurities Can and Do Influence Catalyst
    - Difficult to Share Data
    - Repeat Testing May Be Necessary (\$)

# *General Kinetics Recommendations*

- The government agency most interested should adopt a specification modeled on MIL-P-16005E
  - Form a working group (users and producers)
  - Attack Each Section Separately; Baby Steps
- Important
  - Prep for Delivery (To Prevent Accidents)
  - Requirements
    - Use MIL-P-15006E Levels
    - Best Scenario for Comparison to Historical Catalyst Data
  - QA (May Adopt Modern Methods at Vendor Discretion)

# *Present Work*

- General Kinetics Awarded SLI Contract
  - Testing of 98% H<sub>2</sub>O<sub>2</sub> begins Sept 2001
  - Experimentally determine influence of today's fluid on catalyst bed
  - Look at influence of stabilizers and impurities on catalyst life
- Stabilizers
  - Tin, Phosphate, Nitrate
- Impurities
  - Aluminum, Carbon, Stainless Elements (Ni, Cr, Fe)
- Testing levels set by GK experience, public information from 50-60's and fluid vendor information
- Looking for other information

# *Conclusions*

- Prior US H<sub>2</sub>O<sub>2</sub> Specifications are Canceled
- Specification is Necessary for Future Work
  - No Common Basis for User/Producer to Use
  - Difficult to Share Test Data
  - Eliminate Unnecessarily Redundant Work
  - Provide for Safest Possible Transportation and Handling
- A Government Agency Must Adopt & Spear Head a New Specification
- NASA SLI/GK has begun with testing 98% Impurity/Stabilizer Level
- Use MIL-P-16005E as “Model” for New Specification