Aerosol 101: Formulation Considerations & Testing Methods

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Part I: Formulation Considerations

Part II: Common Aerosol Test Methods

Part III: Basic Aerosol Lab Setup
Part I

Formulation Considerations
Basic Aerosol Formula & Components

- Carrier / Solvent
- Emulsifier / Surfactant
- Additives / Actives
- Corrosion Inhibitor(s)
- Propellant
- Can
- Valve
- Actuator
- Dip Tube
- Accessories (ext. tube, agitator, etc.)
How To Begin?

• Determine what the customer REALLY needs. Learn to LISTEN without bias. Ask questions. Try to determine a customer’s unmet needs.
• Obtain information on comparable products.
• The internet is a great information source for:
  - Safety Data Sheets (MSDS)
  - Technical Data Sheets
  - Regulatory information
  - Competitor Pricing information
• Obtain samples of comparable products if possible.
• Consult with your component and chemical vendors.
Performance and Customer Expectations

- Appearance (spray pattern, foam appearance, viscosity, etc.)
- Function (product matching vs. product improvements)
- Shelf life (compatibility – concentrate, valve gasket, can)
- Pricing (raw materials, components, labor costs, transport, etc.)
- Component availability and lead times.
- Regulatory issues (banned chemicals, VOCs, Prop 65, etc.)
Regulatory Constraints

- Chlorofluorocarbon ban.
- VOC/MIR Restrictions – EPA, OTC, CARB, etc.
- CA Chlorinated Solvent ban.
- CA Proposition 65.
- NSF Registration – Food Products
- Consumer Product Safety Commission
- FDA Regulations
- EPA Regulations
- National Fire Protection Association
- Occupational Health and Safety Admin. (OSHA)
- TSCA and SARA Listed Chemicals (US)
- REACH / RoHS Listed Chemicals (EU)

Note: This is FAR from being a complete regulatory list.
Production Limitations and Plant Safety

- Appropriate compounding equipment (tanks, mixers, etc.).
- Compounder training and expertise.
- Plant ventilation (flammable and/or toxic vapors).
- Grounding and spark suppression equipment.
- Batch heating and chilling capability.
- Filling equipment limitations (viscosity).
- Gas house equipment limitations.
- Manufacturing efficiency (downtime between runs).
- Hazardous waste generation.
Cost Issues

- Determine a realistic cost point.
- Consolidate raw materials to increase volume.
- Use stock inventory when possible.
- Container and component expense.
- Propellant expense.
- Testing expense (specifications, field trials, QC, etc.).
- Production line down time.
- Dedicated equipment and storage.

“Greed Is Good” - Gordon Gekko
Avoid The Formulator Triangle

DON’T LOSE SIGHT OF YOUR GOAL!
Part II
Common Aerosol Test Methods
**pH**

- A pH range of 9 to 10.5 is optimal for unlined steel containers.
- A pH range of 4.5 to 8.5 is optimal for aluminum containers.
- pH less than 8 problematic for unlined steel containers.
- pH can drift over product lifetime.
- Do not depend on container linings alone.
Density and Weight

• Difference between volume and weight.
• Use density of concentrate and propellant to determine concentrate, propellant and headspace volume.
• Label fill volumes are based on concentrate and “liquefied” propellant volumes*.

**Recommended Headspace Volumes**

- Hydrocarbon  
  5% minimum
- Fluorocarbon  
  5% minimum
- CO₂*  
  20-25% optimal (15% maximum)
- N₂  
  40-50% optimal

*Empirical data indicates that 1 gram of CO₂ increases the liquid volume by 1cc.
Viscosity and Rheology

• There are many types of test equipment and methods for determining product viscosity and rheology. They all tend to involve either rotational friction or capillary extrusion practices.

• Variations in viscosity and rheology can have dramatic effects on the following:
  - Time and effort spent compounding and filling.
  - CO₂ absorption.
  - Spray Pattern.
  - Foam Stability.
  - Sprayout Appearance.
  - Low temperature usability.
Viscosity and Rheology (cont.)

- Rotational Viscometer
- Kinematic Capillary
- Zahn Cup
Moisture

- Karl Fischer commonly used for ppm determination.
- High moisture (>1000 ppm) can lead to interior rust and corrosion.
- Careful! – Moisture as low as 100 ppm can cause can failure.
- Product performance and stability can be affected (anti-static sprays).
Flash Point

- Two basic types: open cup and closed cup.
- Product flammability and safety issues.
- Production constraints.
Crimp Dimensions

Crimp Depth and Diameter
- Proper seal between valve and container “curl”.

Stem Height
- Proper clearance between top of actuator and cap.
- Proper clearance between valve stem and actuator (dome spray caps).

*Obtain proper crimp dimensions from your valve vendor.
Crimp Dimensions (cont.)

Diameter Gauge  
Depth Gauge  
Stem Height Gauge
Department of Transportation
Subpart G: Gases; Preparation and Packaging

Section 3 (v) Each container must be subjected to a test performed in a hot water bath; the temperature of the bath and the duration of the test must be such that the internal pressure reaches that which would be reached at 55 °C (131°F) (50°C (122°F) if the liquid phase does not exceed 95% of the capacity of the container at 50°C (122°F)). If the contents are sensitive to heat, the temperature of the bath must be set at between 20°C (68°F) and 30°C (86°F) but, in addition, one container in 2,000 must be tested at the higher temperature. No leakage or permanent deformation of a container may occur.
What does it mean for a “typical” aerosol?

- **AFTER** passing through the water bath, the internal pressure of product containers must reach a pressure equal or greater than the internal pressure of the product when at equilibrium at 50°C (122°F). Note: If liquid phase does not exceed 95% of container capacity at 50°C (122°F).

- There must be no leakage or permanent deformation.

- Water bath temperature and dwell must be sufficient so that ALL manufactured units are subject to the above test condition before transport.

*For “non-typical” aerosols consult the regulation.*
Determination of Aerosol Flammability

• Flame extension test – being phased out
• Open drum test – being phased out
• Ignition distance test – being phased in by GHS
• Enclosed space ignition test – being phased in by GHS

• Two aerosol flammability ratings addressed by GHS:
  - Flammable Aerosol (Category 1)
  - Extremely Flammable Aerosol (Category 2)
Determination of Aerosol Flammability (cont.)

Flame Extension Test

Enclosed Space Ignition
Heat of Combustion

- NFPA 30B - Flammable and Combustible Liquids Code: Manufacture and Storage of Aerosol Products. Dictates the type of fire suppression system required for aerosol storage.
- Level 1 Aerosols require less stringent fire suppression.
- Level 3 Aerosols require the most stringent fire suppression.
- Aerosol level classification must be on shipping containers.
- Careful! - There is not necessarily a correlation between the aerosol level and the aerosol flammability.
Heat of Combustion (cont.)

Flammability level of aerosols is determined by the heat of combustion of the product contents:

- Level 1 Aerosols. Total chemical heat of combustion less than or equal to 8,600 Btu/lb (20 kJ/g).
- Level 2 Aerosols. Total chemical heat of combustion that is greater than 8,600 Btu/lb (20 kJ/g), but less than or equal to 13,000 Btu/lb (30kJ/g).
- Level 3 Aerosols. Total chemical heat of combustion is greater than 13,000 Btu/lb (30 kJ/g).
Heat of Combustion (cont.)

- The chemical heat of combustion can be determined using a bomb calorimeter or can be calculated using information from reference sources.
Spray
Discharge Rate / Characteristics / Pattern

- Concentrate viscosity & rheology.
- Propellant choice and amount.
  - bag on valve (BOV)
  - piston container
- Valve choice.
  - vapor tap
  - 360° valve
- Actuator choice
- Temperature
Aerosol Particle Size

- Spray characteristics may be varied by changing the concentration or type of propellant, valve, actuator, or solvent.
- The spray characteristics of various systems are described as very fine, fine, medium, coarse streamy and stream.
- Consult with your valve vendor regarding aerosol particle size analysis.
Aerosol Particle Size (cont.)

- Typical Cloud Droplet: (20 microns)
- Large Aerosol Particle: (100 microns)
- Typical Raindrop: (2 millimeters)
- Small Aerosol Particle: (1 micron)
Aerosol Particle Size (cont.)

- Particles as large as 100 μm and as small as 5 μm are trapped in the nose.
- Those 2 to 5 μm in size are deposited somewhere in the respiratory tract proximal to the alveoli.
- Deposition in the alveoli is 90 to 100 per cent for particles 1 to 2 μm in size.
Aerosol Particle Size (cont.)

• Consider the nature of your product when analyzing particle size:
  - Bronchial dilator for asthma relief – 1 to 2 micron particle size - good.
  - Silica particles aspirated into lungs – less than 5 micron particle size – bad.
  - Fluorosurfactant based degreaser – 1 to 2 micron particle size - very bad.
    (change in alveoli surface tension leading to chemical pneumonia)

• Aerosol particle size can have an effect on Flame Projection:
  - large particles and stream sprays tend to be less flammable than small particles or mist type sprays.
Concentrate Particle Size

• Must have adequate clearance for LARGEST particles to pass through the valve stem AND the actuator orifice.
• Recommend no larger than 50 µm.
• Production can filter concentrate to prevent valve clogging.
• Careful….
  - particles can coalesce over time creating a valve clogging issue after manufacture.
  - particles can precipitate and adhere to bottom of container.
• Perform adequate stability testing.
Compatibility/Stability Testing

- Two types of stability testing:
  Electrochemical and Long Term Static
- Electrochemical testing for rapid screening.
- Long Term Static over several months/years.
  - Elevated temperature (120°F) AND room temperature stability tests should be performed concurrently.
  - Low temperature testing (~45°F) is recommended for viscous products, products prone to crystallization and/or precipitation.
- Watch for valve gasket swell and hardness issues.
Miscellaneous Testing

- VOC / MIR
- Gasket Swell/Hardness Testing
- Foam Density and Stability
- Active Ingredient Analysis
  - titrations
  - gas chromatography
  - HPLC
  - FTIR
- Microbial Testing
- ... and many more.
Part III
Basic Aerosol Lab Setup
Explosion Proof Fume Hood
Lab Propellant Filler
Valve Crimper
Compatibility Bottles
Other Equipment

• Inert compressed gas source (nitrogen).
• Appropriate gas pressure regulator(s).
• Explosion proof oven (Stability Testing).
• Explosion proof cooler (Stability Testing).
• Aerosol pressure gauges.
• Aerosol valve crimp and stem height gauges.
• Aerosol valve adaptors (filling and pressure check).
General Safety Practices for the Aerosol Laboratory

- Smoking is prohibited in the lab!
- Personnel shall be properly trained in the safe and efficient operation of fire extinguishers, safety showers, and other safety equipment.
- Personnel shall be properly trained in the proper use and handling of liquefied flammable gases, cryogenic gases, and flammable or combustible liquids.
- Proper clothing such as 100% cotton lab coats should be worn to prevent static accumulation or discharge.
- Proper personal protective equipment such as safety glasses or goggles, face shields, and protective gloves or clothing shall be used as required by the Plant Safety Policy.
- Safety Checklists should be used for start-up, operation, and shut-down of equipment. This is especially important where mechanical gassing equipment is used in the aerosol laboratory.
- Propellant gas supply cylinders must be maintained in a protected outside area and should be brought into the Laboratory only for appropriate reasons and for brief periods under the supervision of the Laboratory Director. The largest size propellant cylinder allowed in the Aerosol Laboratory is a 5 gallon capacity (20# propane) cylinder.
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General Safety Practices for the Aerosol Laboratory (cont.)

- Cylinders must be chained or strapped in place, and must be capped when not in use unless otherwise protected.
- Always ground propellant cylinders when in use.
- Mechanical gassing installations must have gas detection and ventilation exhaust systems. Pilot Laboratories must meet the requirements of NFPA 30B.
- Propellant gases (liquids under pressure) must always be handled in a sealed system that is checked periodically for signs of leakage.
- Strictly control the accumulation of discarded or leaking aerosol containers. Provide proper exhaust ventilation to prevent accumulation of flammable vapors.
- Filled aerosol cans should be checked for possible leakage. The hot water bath used to test aerosol dispensers should have an exhaust hood above it to capture any released vapors. A perforated or wire metal mesh cover above the bath should be strong enough to withstand foreseeable container rupture.
- Aerosol retain storage rooms must have adequate air circulation.
- Routes of egress must be kept clear and free from accumulations of corrugate, filled cans, and other products.
General Safety Practices for the Aerosol Laboratory (cont.)

- The amount of flammable material stored and handled should be kept to a minimum. The smaller the amount of fuel, the smaller the fire in case of an accident.
- Ventilation is the best general precaution against fires resulting from flammable gases or vapors.
- All sources of ignition should be eliminated or controlled where possible.
- Hoods that fail to meet manufacturers’ standards should be cleaned out or otherwise repaired. A good, efficient, explosion-proof exhaust hood should be used for routine operations such as the exhausting of aerosol cans, provided that flammable gases and liquids are not introduced to the environment at an excessive rate.
- Refrigerators, cold rooms, and deep-freeze cabinets should be explosion-proof. Doors should be held shut be magnetic studs, so that they can readily blow open if a flash fire or explosion does take place inside the enclosure.
- Aerosol Formulation and Product Development Laboratories may be considered Pilot Labs and may require further engineering controls including additional exhaust ventilation, explosion relief vent panels, Class 1, Division 1 or 2 electrical code, gas detection systems, sprinkler systems, etc. Consult NFPA 30B for additional information.

Source - Diversified CPC International, Inc.
Recommendations for Burette Pressure Filler Operations

- Only Trained Personnel shall operate the Burette Pressure Fillers.
- Bond and Ground Nitrogen Cylinder, Propellant Cylinder and Burette Pressure Filler.
- Assure that the Burette Pressure Filler is properly mounted and secured.
- Secure Nitrogen and Propellant tanks with chains or straps.
- Never use Liquid Nitrogen to pressurize a Burette Pressure Filler. Liquid Nitrogen is at a temperature of 320 degrees BELOW zero F (-160 C) under normal atmospheric pressure. This low temperature will shatter carbon steel, glass, etc. and cause severe burns.
- Always wear Safety glasses (or Goggles) and Full Face Shield when operating a Burette Pressure Filler.
- Inspect the Burette for visible damage prior to use. Replace the Burette if there is evidence of nicks or chips in the glass.
- Transfer of Propellants must be performed:
  a) Gas House or Charging Room
  b) Aerosol Pilot plant -or -Pilot Lab
  c) Outdoors in a ventilated area -away from sources of ignition
  d) In a well ventilated Lab Hood equipped with Combustible Gas Sensors (where allowed)
Recommendations for Burette Pressure Filler Operations (cont.)

• While filling the Burette with Propellant Liquid - it may be necessary to vent off some vapors. SLOWLY vent the Propellant vapors to avoid accumulation of flammable vapors.
• Make sure that you are transferring an accurate volume of propellant into the aerosol can by weighing the can after filling.
• Do not completely empty the Burette of Propellant Liquid when filling the aerosol can, as the Nitrogen gas may enter the can and affect the properties of the propellant in the aerosol package.
• Use common sense and caution when operating a Burette Pressure Filler.

Source - Diversified CPC International, Inc.
LEARN FROM YOUR MISTAKES!!
QUESTIONS?