Introduction

Frequently, formulators are faced with the challenge of delivering an effective, quality product within a short period of time.

Formulating an aerosol product is far more complex than a liquid or liquid spray product. When you talk about an aerosol formulation the entire package must be considered, the concentrate, container, valve/actuator, and the propellant.

Each component of the aerosol formula is equally important and must be fine tuned to make the product functional. The following topics are by no means inclusive or applicable to all situations, but can be used as a starting point.
• Topics that will be reviewed are:
  - Formulation Cost
  - Aerosol Container Types
  - Raw Material Selection
  - Formulation Types
  - Regulatory Issues
  - Container Corrosion
  - Fill Levels
  - Propellant Selection
  - Spray Characteristics
  - Stability Testing
The most important requirement of any project is to determine how much money is available for the aerosol formula. Usually the only exception to this is when the product is unique or first to market. The pricing information will usually come from Marketing or Sales. If your product is a knock-off, a pricing structure for the product already exists. Focus groups are often used by marketing to determine consumers reaction to a new product concept and what price they would be willing to pay.

Always use existing raw materials if possible. By using existing inventory, better pricing can be realized when purchasing at a higher volume. This also helps keep the raw material inventory costs at a minimum.
FORMULATION COST

- Type of aerosol container: A non-specification can is the least expensive. 2P or 2Q cans are more expensive and adding a seam vent adds more cost. Piston and barrier bag aerosol containers are more expensive. The aerosol formulation pressure measured at 130°F will determine what aerosol container can be used for the product.

- Valve/actuator and cap: Costs are fairly uniform with these items unless you need a non-stock or specialty item to dispense your product such as a 360° spray valve.

- Type of Propellant used: The cost of the propellant can have either a major or minor impact on the price of the aerosol formulation.
AEROSOL CONTAINER TYPES

• Three piece and two piece metal containers (tin plated steel)
  
  - Unlined Metal Containers: This can is used for solvent based aerosols and used for water based concentrates which contain corrosion inhibitors.
  
  - Lined Metal Containers: This can is used mostly for water based applications. Solvents will usually dissolve these linings. Water based formulations containing over 19% Dimethyl Ether should use an unlined can with a good corrosion inhibitor package. Dimethyl Ether at this level will penetrate the can lining allowing attack of the tinplate. Some of the two piece containers only come lined, therefore stability must be run for solvent blends.
AEROSOL CONTAINER TYPES

- Double Lined Metal Containers: This can is used for water based products where added corrosion protection is required.
  - Interior coatings are normally applied before container fabrication. Common linings are phenolic resin, urethane, or epoxy.

- Single piece Aluminum cans (lined and unlined)
- Plastics containers
- Glass containers (perfume)
- Piston and Barrier Bag containers (gassed from the bottom).
Raw Material Selection

• It is always best to use in-house raw materials.

• Review current and past in-house formulations as a potential starting point. Don’t rediscover the wheel.

• McCutcheon’s publishes a set of books named McCutcheon’s Detergent and Functional Materials. These are excellent references.

• The Internet is very useful for gathering Raw Material literature. Companies now have their own websites.
Raw Material Selection

• Chemical Distributors and chemical manufacturers are an excellent source for securing information on potential raw material components and newly developed raw materials. One can always secure a secrecy agreement to keep information confidential.

• If you are duplicating an existing product, get product samples for analysis and the products Material Safety Data Sheets.

• Natural or synthetic raw materials: Always be open to new ideas. Although the cost of these materials may be high, they may be cost effective in the finished aerosol formulation.
Formulation Types

• **Water Based (Emulsions, Dispersions):**
  
  – Water based products are normally contained in lined and double lined cans (phenolic resin, urethane, or epoxy linings). They are also contained in unlined cans if an effective corrosion inhibitor is used.

  – Propellants normally used in aqueous products are Hydrocarbon, Hydrocarbon Blends, Dimethyl Ether, Hydrofluorocarbons, and Nitrogen.

  – The only propellant that is not normally used in aqueous formulas is Carbon Dioxide. This propellant in an aqueous medium will form carbonic acid causing potential corrosion problems and can also affect the physical parameters of the finished aerosol product.
Formulation Types

Water Based (Emulsions, Dispersions):

- Because of cost, the majority of water based aerosols are most likely dispensed using a hydrocarbon propellant at a 4 to 10% level.

- Since Dimethyl Ether is soluble in water, if over 19% DME is required to dispense the contents, a good corrosion inhibitor must be used because DME will penetrate can linings allowing attack of the tinplate. Nitrogen is less commonly used.

- Corrosion Inhibitors, anti-oxidants, and biocides are typically used in aqueous formulas.
Formulation Types

- **Solvent Based (Water in Oil, Dispersions):**
  - Unlined containers are normally used because most solvents will dissolve the interior coating of the can.
  - If you have a moisture content of greater than 0.1% present in the concentrate, a corrosion inhibitor will most likely be necessary. In certain situations, even a moisture content less than 0.1% could cause interior can corrosion.
  - Propellants used in solvent formulas are Hydrocarbons, Hydrocarbon blends, Hydrofluorocarbons, DME, Carbon Dioxide, and Nitrogen.
Solvent Based (Water in Oil, Dispersions)

- Solvent Formulas will normally require a higher level of the liquified gas propellant. Propellant levels as high as 1/3 of the Net Content of the product may be necessary to completely discharge the can. It is normal for the DME, Hydrofluorocarbon and Hydrocarbon propellants to act as solvents in these formulas.

- Carbon Dioxide levels in solvent formulas will run between 2 to 7% and Nitrogen will run about 0.5 to 2%. The saturation level of Carbon Dioxide in the concentrate is greater than that of Nitrogen.
Regulatory Issues

DOT Regulations for Aerosol Containers
CFR, Title 49, Section 173.306

• Containers of 4 fluid ounces (118.3 mL) overflow capacity or less are exempt from the following requirements, provided they hold non-hazardous materials.

• Liquid content of the concentrate and gas must not completely fill the container at 130°F.

• Container must be capable of withstanding, without bursting, a pressure of one and one half times the pressure of the contents, when at 130°F equilibrium. Distortion is acceptable.
Regulatory Issues

DOT Regulations for Aerosol Containers
CFR, Title 49, Section 173.306

• Container must not be used for contents with pressures that exceed 180 psig at 130°F.
  – DOT 2P CONTAINER: If the content pressure exceeds 140 psig but does not exceed 160 psig at 130°F a DOT Specification 2P container is to be used.
  – DOT 2Q CONTAINER: If the content pressure exceeds 160 psig but does not exceed 180 psig at 130°F a DOT Specification 2Q container is to be used.
  – Non Specification Containers require a 210 psig burst resistance min..
DOT Regulations for Aerosol Containers
CFR, Title 49, Section 173.306

- The container must not exceed a capacity of 61 cubic inches capacity (one liter).

- 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 (130°F) or 50°C (122°F) if the liquid phase does not exceed 95% of the container at 50°C (122°F).
Biodegradability: Is Biodegradability one of the product requirements? What is the definition of Biodegradable? When referring to biodegradability, readily and inherently biodegradable are terms that are widely used in industry today.

- **Readily Biodegradable:** A material is considered to be Readily Biodegradable if it shows a $>60\%$ degradation within a 28 day period. Readily Biodegradable is preferred because it does not require a long term bio-remediation.

- **Inherently Biodegradable:** This means that the material will eventually degrade.
ASTM Definition of Biodegradable: They have defined Biodegradable as a function of degree of degradation, time, and test methodology. ASTM D5864 describes inherently and readily biodegradable.

- Inherently Biodegradable: 20 to 60% conversion of CO2 within 28 days. The rate of Biodegradable Activity.

- Readily Biodegradable: >60 to 100% conversion of CO2 within 28 days. The rate of Biodegradable Activity.
Volatile Organic Compounds (VOC’s):

- It is no longer just California! A number of Northeastern States have already adopted legislation similar to that of the California Air Resource Board (CARB). The OTC States (Ozone Transport Commission-Virginia to Maine) and the Ladco States (Illinois, Indiana, Michigan, Ohio and Wisconsin) are making efforts to reduce air pollution by reducing the VOC’s in consumer products.
## REGULATORY ISSUES: NEW 2003 CARB VOC LIMITS

<table>
<thead>
<tr>
<th>Product Type</th>
<th>Effective Date</th>
<th>VOC Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive Brake Cleaners</td>
<td>12/31/2010</td>
<td>10</td>
</tr>
<tr>
<td>Carburetor or Fuel Injection Air Intake Cleaner</td>
<td>12/31/2010</td>
<td>10</td>
</tr>
<tr>
<td>Carpet and Upholstery Cleaner (Aerosol)</td>
<td>12/31/2010</td>
<td>50</td>
</tr>
<tr>
<td>Engine Degreaser (aerosol)</td>
<td>12/31/2010</td>
<td>10</td>
</tr>
<tr>
<td>Product Description</td>
<td>Effective Date</td>
<td>VOC Standard</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Fabric Protectant (non-aerosol)</td>
<td>12/31/2010</td>
<td>1</td>
</tr>
<tr>
<td>Glass Cleaners (Aerosol)</td>
<td>12/31/2012</td>
<td>10</td>
</tr>
<tr>
<td>Motor Vehicle Wash (non-aerosol)</td>
<td>12/31/2010</td>
<td>0.2</td>
</tr>
<tr>
<td>Multi-Purpose Solvent</td>
<td>12/31/2013</td>
<td>3</td>
</tr>
<tr>
<td>Paint Thinner</td>
<td>12/31/2013</td>
<td>3</td>
</tr>
<tr>
<td>Spot Remover (Aerosol)</td>
<td>12/31/2010</td>
<td>15</td>
</tr>
</tbody>
</table>
The role of the chemist is no longer to just formulate, but to ensure that the product being developed uses chemicals that are safe for consumer and environmental use. If the product will be used in the home there is a chance of children being exposed to the product. If used in industry, the function of the finished product may dictate what hazardous materials are used. It is also the responsibility of the chemist to ensure that the product is properly labeled according to federal and state regulations. If your company has a Regulatory Department, they will normally handle labeling issues.
**Flammability:** If you need a fast drying or evaporating formula, then the odds are that you will develop an Extremely flammable aerosol. The Flammability of an aerosol is primarily determined by a Flame Extension Test, not by flash point. It is not feasible to run a flash point with propellant present.

- Extremely flammable contents of a self-pressurized container means contents of a self-pressurized container that, when tested by the method described in Sec. 1500.45, a flashback (a flame extending back to the dispenser) is obtained at any degree of valve opening and the flashpoint, when tested by the method described in Sec. 1500.43a, is less than 20 deg.F (-6.7 deg.C).
Regulatory Issues: Product Hazards

- Flammable contents of self-pressurized container means contents of a self-pressurized container that, when tested by the method described in Sec. 1500.45, a flame projection exceeding 18 inches is obtained at full valve opening, or flashback (a flame extending back to the dispenser) is obtained at any degree of valve opening.
Regulatory Issues: FLAME EXTENSION APARATUS
Regulatory Issues: Product Hazards

• **Toxic:** means any substance which has the capacity to produce personal injury or illness to man through ingestion, inhalation, or absorption through any body surface.

• **Highly Toxic.** These products can produce death. An example is methanol which must be labeled Poison with a skull and crossbones symbol and a statement of “Can not be made non-poisonous”.

• **Corrosive:** means any substance which in contact with living tissue will cause destruction of tissue by chemical action, but shall not refer to action on inanimate surfaces.
Regulatory Issues: Product Hazards

- **Irritant:** means any substance not corrosive which on immediate, prolonged, or repeated contact with normal living tissue will induce a local inflammatory reaction.

- **Cancer/Reproductive Harm:** If a product sold in California contains a California Proposition 65 chemical, the manufacturers must add the following statement to the product label; “This product contains chemical(s) known to the state of California to cause cancer and/or reproductive toxicity”.

- **Pressurized Container:** All aerosols have the potential to explode or burst when exposed to heat, flame, or sunlight.
Container Corrosion

Corrosion: Corrosion is not just an interior can problem. It occurs both on the interior and exterior of the can. Common corrosion promoters are chloride and hydrogen ions. The presence of chloride ions can cause container breakout within a short period of time. Tinplate will also corrode under high humidity conditions. Free water must be present for this corrosion to take place. Corrosion is a major problem that could lead to product recalls, order cancellations, bad press, and potential lawsuits.

- Exterior Corrosion: Uninhibited hot tank water, water left in the valve cup, or storage of the aerosol container in a high humidity area, especially close to the ocean, will promote can corrosion.
Container Corrosion

- **Crevice Corrosion**: Also referred to as seam corrosion, the weld seam, top and bottom seams.

- **Pitting Corrosion**: Pitting corrosion is extremely localized and an intense form of attack which can lead to can perforation.

- **Stress Corrosion**: This corrosion is localized at the stress or worked areas of the aerosol can, such as the dome chimes or valve cup bends.
Container Corrosion

• Seven areas of interior corrosion:
  – Vapor Phase crevice corrosion
  – Vapor Phase corrosion
  – Interfacial corrosion
  – Weld corrosion
  – Liquid phase corrosion
  – Liquid phase crevice weld corrosion
  – Liquid phase weld corrosion
Container Corrosion:
Interior Corrosion
• **Corrosion Inhibitor Systems:** Corrosion inhibitors are formulated into the concentrate to treat these areas of interior corrosion. It is not unusual to use an inhibitor for the liquid phase and one for the vapor phase. Typical corrosion inhibitors are sodium nitrite, morpholine, triethanolamine, and ammonia. As a general rule, sodium nitrite and amine types of corrosion inhibitors are not used together because there is a possibility that the combination may form N-nitrosamines. Corrosion is also affected by the pH of the contents. Extreme pH’s below 5 and above 10 will commonly promote corrosion.
Even with the use of inhibitors and adjustment of the pH, corrosion could still take place. D.I. Water should always be used in aerosol formulations because all traces of the chloride ion have been removed which will promote corrosion.
Fill Levels

Aerosols are filled according to Net Weight, which includes the concentrate and propellant. Since aerosols can not be poured out of the container and checked for volume, weights are used.

- **Head Space:** This is the area between the liquid phase and the bottom of the valve. Compressed gases usually require a min. of 15% headspace whereas hydrocarbon propellants usually require less.

- **An Equilibrium Vapor Pressure** at 130°F of the filled aerosol product will determine whether the liquid contents needs to be reduced or a vapor depressant is necessary.

- **Net Content:** The aerosol container is required to dispense the Net Weight stated on the label.
Propellants provide the power to dispense the aerosol product. They also influence the form in which the product is discharged and they are either liquidified gases or compressed gases.

**Hydrocarbon and Hydrocarbon Blends:**

- A-17: n-Butane
- A-31: Isobutane
- A-46: Propane/Isobutane (15.1/84.9)
- A-70: Propane/Isobutane (41.9/58.1)
- A-108: Propane
## Properties of Hydrocarbon Propellants

<table>
<thead>
<tr>
<th></th>
<th>Propane</th>
<th>Isobutane</th>
<th>n-Butane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor Pressure @ 70 F</td>
<td>108 psig</td>
<td>31 psig</td>
<td>17 psig</td>
</tr>
<tr>
<td>Flash Point</td>
<td>-156°F</td>
<td>-117°F</td>
<td>-101°F</td>
</tr>
<tr>
<td>Solubility in water @ 70 F</td>
<td>0.01% by Wt.</td>
<td>0.01% by Wt.</td>
<td>0.01% by Wt.</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>-43.7 F</td>
<td>10.9 F</td>
<td>31.1 F</td>
</tr>
<tr>
<td>Kauri-butanol Value</td>
<td>15</td>
<td>17</td>
<td>20</td>
</tr>
</tbody>
</table>
Propellant Selection

• **Hydrocarbons and Blends:**
  
  – They are widely used in water based products because they are economical.

  – They are not soluble in water and require a low use level of 4 to 10% of the net content.

  – They provide a constant spray rate throughout the discharge of the concentrate.

  – Hydrocarbon and hydrocarbon blends offer a wide range of spray pressures to achieve the desired spray pattern and discharge rate.

  – Disadvantage is their flammability with a flash point ranging from -101 to -156°F.
Propellant Selection

Dimethyl Ether:

- DME is significantly higher in price than hydrocarbon propellants.
- Classified as a flammable gas.
- It is a very strong and aggressive solvent.
- An advantage of DME is its solubility in and compatibility with aqueous formulas.
- Disadvantage of DME is that in aqueous formulas at levels at or above 19%, the DME will attack the can lining thus requiring a corrosion inhibitor.
Properties of Dimethyl Ether

Vapor Pressure @ 70 F: 63 psig
Flash Point: -42 F

Solubility in Water @ 70 F: 34% by Wt.

Boiling Point: -12.7 F

Kauri-butanol Value: 60
Propellant Selection

Hydrofluorocarbon Propellant

- Major disadvantage of these propellants is their cost.
- Hydrofluorocarbons are non-flammable.
- As with hydrocarbons and DME, they provide a constant vapor pressure during container discharge.
- **R134a**
  - Advantage of R134a is that it is not listed as a Volatile Organic Compound.
  - Disadvantage of R134a is that it can have a vapor pressure of over 180 psig at 130°F.
# Hydrofluorocarbons

<table>
<thead>
<tr>
<th></th>
<th>HCFC-152a</th>
<th>HCFC-134a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor Pressure @ 70 F</td>
<td>62 psig</td>
<td>70 psig</td>
</tr>
<tr>
<td>Flash Point</td>
<td>0°F</td>
<td>0°F</td>
</tr>
<tr>
<td>Solubility in water @ 70 F</td>
<td>1.7% by Wt.</td>
<td>0.095% by Wt.</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>-11.2°F</td>
<td>-15°F</td>
</tr>
<tr>
<td>Kauri-butanol Value</td>
<td>11</td>
<td>9.2</td>
</tr>
</tbody>
</table>
LIQUIFIED GASES
Propellant Selection

Compressed Gases

- Advantages with the compressed gases are:
  - non-flammable
  - non-toxic
  - environmentally safe
  - inexpensive
  - can be used at low temperatures
• Major disadvantage with compressed gases is that over the use of the product, the delivery rate of the aerosol formulation will drop off.

• Carbon Dioxide is not used with water based products due to formation of carbonic acid.

• They do offer an advantage over the liquified gases at temperatures below 0°F. Usually carbon dioxide will lose half its ambient pressure when stored at 0°F and below. Liquified gases at 0°F and below can exhibit a negative vapor pressure.
## Properties of Compressed Gases

<table>
<thead>
<tr>
<th></th>
<th>Carbon Dioxide</th>
<th>Nitrous Oxide</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vapor Pressure @ 70°F</strong></td>
<td>837 psig</td>
<td>98 psig</td>
<td>-</td>
</tr>
<tr>
<td><strong>Flash Point</strong></td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td><strong>Solubility in water @ 70°F</strong></td>
<td>0.82</td>
<td>0.6</td>
<td>0.016</td>
</tr>
<tr>
<td><strong>Boiling Point</strong></td>
<td>-109°F</td>
<td>-127°F</td>
<td>-232°F</td>
</tr>
</tbody>
</table>
COMPRESSED GASES

![Diagram of compressed gases with pressures 100 psig, 75 psig, and 50 psig.](image)
Spray Characteristics

Spray characteristic are determined by the actuator/valve/propellant and concentrate used. Important contributors are the volume of gas used, the vapor pressure of the propellant, the propellant/ concentrate ratio and the solubility of the propellant in the concentrate.

- **Spray Type:**
  - **Foam:** Long lasting foam, quick breaking foam, or a foam that will cling to vertical surfaces.
  - **Mist:** A very wide circular, donut, or oval type spray pattern. Window cleaners use a mist.
  - **Coarse Spray:** Household cleaners and tar & bug removers will use this type of spray.
Spray Characteristics

- **Stream:** This type of spray would be used by a brake cleaner, choke & carburetor cleaner, or engine degreaser.

- **Bead:** A bead is used to deliver a mastic type of product such as caulking compound, or a construction adhesive used to glue the sub-floor or drywall.

- **Spray Rate:** How fast do you want the material dispensed from the container? You may have a low spray rate because only a small amount of the material is necessary for the job whereas some products may use a high spray rate to help achieve their end purpose.
Spray Characteristics

- The spray characteristics of the aerosol are directly dependent upon the valve and actuator selection. This selection is usually by trial and error. Usually this process can be speeded up by submitting concentrate samples to the valve/actuator companies and requesting valve and actuator samples to achieve your desired spray rate and spray characteristics.
There are two types of stability testing: electrochemical testing and long term static testing. Electrochemical testing provides a limited amount of information but is an effective screening tool. Long term static testing provides the most significant information such as: weight loss, concentrate/propellant saturation changes (vapor pressure measurement), maintaining original spray characteristic, corrosion, and concentrate stability (separation, coagulation, chemical change, color, and odor change). Long term static testing is normally done at a temperature of 120°F, over a period of three months to a year.
Stability Testing

• **Concentrate Stability**: This stability testing is usually run in glass containers because you do not want the container to be a contributing factor to formula’s instability.

• **Product and Container Stability**: Once an acceptable formulation is achieved, start stability testing in the aerosol can, valve, dip tube, and gaskets.
Stability Testing

- **Concentrate and Propellant Stability:** It is always best to prepare an adequate number of samples so that at least one sample can be tested every week for the first three months, then tested every month depending upon the time allotted for stability testing. Weekly tests should be made at ambient temperatures. Testing will involve:
  - Weight loss
  - Pressure testing
  - Spray rate, spray pattern
  - Evacuation of Net Weight
  - Concentrate color and odor
  - Open aerosol container and evaluate for corrosion and dip tube condition.
Stability Testing

Also at least one test sample of the concentrate and propellant should be prepared in a pressure reaction vessel (glass aerosol bottle). With the use of a glass aerosol bottle, it is easy to view whether the product separates and mixes back into solution. A shake well before using may be required on the label directions. Also you can look for color and volume changes in the container which will affect the vapor pressure, thus affecting the spray characteristics.

- **Low Temperature Stability:** If the product is not freeze-thaw stable, directions such as “protect from Freezing” needs to be added to the product label.