Propellants and Solvents

Strategies for the 21st Century

Something Old – Something New

- For many decades aerosol and liquid products in the consumer and industrial markets have experienced a continuous cycle of change mandated by environmental and health concerns. While the industry has responded with the introduction of "next generation" chemicals these have also come under attack leading to addition chemicals being created.
- We will discuss the existing menu of chemicals still available to the formulator and look at the most recent additions that are scheduled to be available in 2013 and 2014.
- Finally, we will discuss formulation opportunities and how new products can utilize these old and new chemicals to meet the current and future needs of the respective markets.

Propellants

- Current Propellants:
- Hydrocarbons – Propane, Isobutane, Normal butane
- HFC's – HFC 134, HFC 152
- Compressed Gases – CO_2, Air, Nitrogen
- Oxygenated – DME
- Blends

- New Propellants:
- Hydrocarbons – Ethane
- HFO's – 1234 ze (Solstice Propellant)

Hydrocarbon Propellants

- Hydrocarbon propellants have been the most common propellant in aerosols since the mid - 70s. In recent years VOC regulations have reduced the percentage of hydrocarbons in aerosols ,but they continue to be the first choice for products around the world. This is due to the following:
- Cost – low when compared to other propellants and solvents and the amount of hydrocarbon, as a percentage of formulation, allows for a reduced unit cost.
- Pressure – Hydrocarbons allow for pressures from 17 psig to 108 psig in the pure chemicals and their blends. In addition hydrocarbons are compatible with all the other old and new propellants.
- Stability – Hydrocarbon are used in solvent based and water based formula. They create stable emulsions and can be used without hydrolysis in water systems.
- Toxicity – Hydrocarbons are on the GRAS list and have high TLVs.
- Environmental – While hydrocarbons are VOCs, they have low MIR values and work well in formulas based on Reactivity.
- Flammability – Hydrocarbons are flammable, but can be blended to reduce the effect on the package.

HFCs

134

- As a propellant 134 has come under fire in recent years due to it’s high GWP. However in reviewing it’s other characteristics, it is obvious that 134 has value as a formulating chemical:
- Cost – Moderate, propellant cost can be reduced by blending.
- Pressure – Good intermediate pressure @70F. Can be increased or reduced by blending.
- Stability – Stable in a wide range of formulas.
- Toxicity – Very low, HFC 134 is currently used in medical devices such as inhalers.
- Environmental – While it does have a high GWP, it is not a VOC or Ozone depleator. When used in appropriate formulations, 134 has a place in many aerosol products.
- Flammability – HFC 134 is considered non flammable and can be used to reduce the overall flammability in aerosols that contain flammable components.

HFCs
152

- HFC 152 – Propellant 152 has become increasing popular in formulated aerosol products and dusters. When we look at its characteristics, it is obvious that this propellant will continue to grow in aerosol products.
- Cost – Moderate
- Pressure – Very similar to 134. A good intermediate pressure that can be blended to achieve higher or lower pressure.
- Stability – Good stability.
- Toxicity – Good TLV, used in dusters, hairspray and other many other products.
- Environmental – Not a VOC, Ozone depleter, and has a low GWP.
- Flammability – Low flammability

Compressed Gases

CO2

- Carbon Dioxide – CO_2 has been a common propellant for many years. Historically its popularity has cycled up and down in response to environmental trends and the marketing strategies of various companies. In todays aerosol market it's commonly utilized in Wasp and Hornet, degreasers, specialty cleaners, and other products that will accept the CO_2 into solution.
- Cost – As an individual chemical, CO_2 is low in cost. However since it is normally used in concentrations of 2-4% the balance of the unit will be comprised of more expensive chemicals increasing the final cost of the package.
- Pressure – CO_2 has a high vapor pressure. This limits it use to very low levels even in those solvents with good Oswald coefficients. It does prove useful in aerosols where the high pressure increases performance at low temperatures such as starting fluids and deicers.
- Stability – CO_2 is used primarily in anhydrous formulas. In any water based formula the CO_2 forms carbonic acid which attacks the metal cans.
- Toxicity – CO_2 has low toxicity.

CO2

- Environmental – While some environmentalists are concerned about the levels of CO2 in the atmosphere, the CO2 utilized in aerosol is obtained by fractional distillation of air. Therefore the CO2 in aerosols does not add to the atmospheric levels and is not an issue for those concerned about global warming.
- Flammability – While CO2 is not flammable, the low levels of CO2 in most aerosols is not sufficient to reduce the overall flammability of the product.

Compressed Gases

Others

- Air – Use of air as a propellant has been practiced in Europe since the 1990s. Recently introduced in the US, the verdict is still out as to the ability of these packages to replace other propellants.
- Nitrogen – Like air which is composed of 78% nitrogen, the use of nitrogen has been tried for many decades. Pure nitrogen has the advantage that the oxygen and CO_2 are removed which eliminates the tendency for oxidation or acid formation. However nitrogen is more expensive and is high pressure with low solubility in many solvents.

Oxygenated

DME

- DME – Dimethyl ether was initially utilized in the US in the 1970s. Since then it has grown in volume for use in both water and solvent based systems. Being a good solvent, DME is unique as a propellant which tend to have low KB values and are usually poor solvents outside their chemicals groups.

New Propellants

Solstice Propellant

- The environmental pressure on propellants has been continuous since the middle of the 20th century. We have seen the elimination of the CFCs, HCFCs, attack on the HFCs, and increasing restrictions on hydrocarbons and DME under VOC regulations.
- Responding to the need, Honeywell has introduced a next generation propellant known as 1234 ze. Solstice propellant falls into a new class of propellants and solvents based on an unsaturated fluorinated base molecule, thus HFO, Hydro-Fluoro-Olefin name. This new propellant has impressive credentials in that it is not a VOC, has a low GWP, and is considered non flammable under DOT definitions.
- With a vapor pressure of 47 psig@70F, it falls into the midrange of propellants and can be blended to achieve higher or lower pressures. Overall the prospects for this propellant are promising.

Hydrocarbons

Ethane

- Ethane is a common chemical though many people may not know of it. Ethane is a saturated hydrocarbon and is a component in natural gas and in the hydrocarbon propellants. In recent years Ethane has become available as a purified chemical suitable for use in aerosol products.
- Having a pressure of 543 psig @70F Ethane falls between CO2 – 869 psig@70F and Propane – 110 psig @70F. In addition Ethane is soluble in most solvents to the extent that 4 – 10% can be used in an aerosol formulation.
- From an environmental stand point, Ethane is not a VOC or Ozone depleator, has a low GWP, and has a good TLV.
- While Ethane is flammable, it can be incorporated into many flammable formulations and it's flammability can be reduced or eliminated by proper blending with other propellants and solvents.
- With its greater solubility, Ethane can produce a better spray pattern than a comparable CO2 product and the higher volume of propellant will give greater protection from propellant exhaustion.

Blends

- Blended propellants are the key to making current formulas work efficiently. Prior to the 1970s, the industry had available numerous propellants and solvents to formulate the variety of products required by consumers and industry. However in addressing environmental and toxicity concerns, the regulators did not effectively regulate chemicals, they eliminated groups of chemicals without regard to the impact on these products and the consumers. The aerosol industry has been able to create replacements, but only through the use of propellant and solvent blends.
- For many years formulators have used the flexibility of the hydrocarbon propellants to create blends with pressures from 17psig to 110 psig. In addition blends of hydrocarbons, DME, HFCs, and CO_2 have allowed these products to thrive.
- When formulators are designing a new product, they must address a number of characteristics to achieve a product that marketers can offer to the public and that the public will purchase. In addition that product must comply with federal and state regulations to meet VOC requirements and not contain some proscribed chemicals.

Blends

- There are various approaches in designing a new formulation. However most will address some consistent parameters:
- 1. cost
- 2.flammability
- 3.solvency
- 4.evaporation rate
- 5. regulatory/VOC/GWP
- 6. toxicity
- 7.pressure
- 8.stability

Cost

- Cost will vary per product, but are generally ranked as follows:
- HFO Solstice Propellant
- HFC 134a
- HFC 152a
- Ethane
- DME
- Propane, Isobutane, Normal butane(A-108, A-31, A-17)
- Nitrogen/Air
- CO2

Cost Comparison

108psig Blend

- Solstice Propellant - $8.50/lb.*
- Ethane - $2.00/lb.

- Blend - $7.72/lb.

- *lower pricing expected in late second quarter

31psig Blend

- Solstice Propellant - $8.50/lb.*
- A-17 - $.58/lb.

- Blend - $4.31/lb.

Pressure

- Nitrogen – 492psig@ -232.5F   1600psig@70F(estimate)
- CO_2 – 859.4 psig
- Ethane – 543 psig
- Propane – 109.3 psig
- HFC 134 – 71.0 psig
- HFC 152 – 63.9 psig
- DME – 61.3 psig
- Solstice Propellant – 47 psig
- Isobutane – 31.1 psig
- Normal butane – 16.9 psig

Pressure Blends

HFO/Hydrocarbon/+

- Solstice – 47 psig
- Ethane – 543 psig

- 108psig blend
- 88% 1234ze
- 12% Ethane
- Cost - $7.72

HFO/Hydrocarbon/-

- Solstice – 47psig
- A-17 – 17psig

- 31psig blend
- 47% 1234ze
- 53% A-17
- Cost - $4.31

Solvency

- KB Values
- DME – 60
- Normal Butane – 20
- Isobutane – 18
- Propane – 15
- Ethane - 12
- HFC 152 – 11
- HFC 134 – 9.2
- Solstice Propellant- 9

Solvency Blend
Adhesive

- DME –   30%   60
- A-70 -   40%   16
- HFC 152 – 30%   11
  - Better solvent
  - Lower VOC

Flammability

HFC 134 – non flammable, can suppress other flammables

Solstice Propellant – considered non flammable

CO_2 – non flammable, practical levels of use reduce the ability to suppress other flammables

Nitrogen – non flammable, low concentrations in aerosols are not sufficient to suppress flammables

HFC 152 – flammable, flammability can be reduced by appropriate additives

Hydrocarbons -ethane, propane, isobutane, normal butane – flammable

DME – flammable, requires modification of equipment to be used in aerosols

Flammability Blend

- 88% Solstice Propellant
- 12% Ethane
- Reduced cost - $7.72/lb.
- Non VOC
- Low flammability/no flammability
- Low GWP

Flammability 2

- 50% Solstice Propellant
- 50% HFC 152
- Non VOC
- Pressure 55psig@ 70F
- Lower flammability
- Lower cost - $5.26/lb.
- Lower GWP
- Lower unit cost

Regulatory

- Solstice Propellant – non VOC, GWP -6
- HFC 152 – non VOC, GWP – 140
- HFC 134 – non VOC EPA* - GWP – 1300
- Ethane – non VOC (MIR - .26) – GWP – 2.9
- Propane – VOC (low MIR - .46) – GWP – 3
- DME – VOC (MIR – 1.02) – GWP - 1
- Normal Butane – VOC (MIR 1.08) – GWP – 2.3
- Isobutane – VOC (MIR – 1.17) – GWP – 3.3

- * HFC 134 while classified by EPA as a non VOC, has been exempted in California for specific uses only.

Regulatory blend

- MIR - .70

- Ethane – 46%
- A-17 - 54%
- Blend – 259 PSIG@70F
- Cost - $1.23/lb.
- Unit cost potentially lower

Toxicity

- There are no issues for the toxicity of these chemicals. TLVs are high for all.

Stability

- With the exception of CO_2, the remaining propellants are used in solvent and water based formulas.
- CO_2 is not suitable for water based formulas due to the formation of carbonic acid.
- It is recommended that all formulas be tested prior to commercial release.

Solvents

- HFC 4310 – DuPont Vertrel XF
- HFC 365 – Solvay Solkane 365
- 1,2 Trans Dichloroethylene – DCPC
- Solstice PF – Honeywell
- HFX 110 – DuPont Vertrel

Costs

- 1, 2 Trans Dichloroethylene
- HFC 365
- Solstice PF
- HFC 4310(Vertrel XF)
- HFX 110

Evaporation rates

- Solstice PF
- HFC 4310(XF), HFC 365, 1,2 Trans Dichloroethylene
- HFO 110 (HFX 110)

- With the exception of HFX 110, all are fast evaporating solvents

Evaporation Ladder*

- Propellant – HFC 134 or HFX 1234ze
- Solstice PF/Vertrel XF
- HFC 365 (Flammable)
- 1,2 Trans Dichloroethylene (Flammable)
- HFX 110
- * Aerosol will exhibit low or no flammability

Solvency

- 1,2 Trans Dichloroethylene – KB 117
- Solstice PF – KB 25
- HFC 365 – KB 14
- HFC 4310 – KB 9
- HFX 110 – less than 10

225 Replacement

- Solstice PF - 10%
- Vertrel XF(4310) – 10%
- Solkane 365 - 55%
- Trans - 25%

- KB – 40
- Cost - $5.78/lb.

141b Replacement

- Vertrel XF – 10%
- Solstice PF – 20%
- Solkane 365 – 25%
- Trans - 45%

- Cost - $5.62
- KB - 61

Flammability

- HFC 4310 – non flammable**
- HFX 110 – non flammable, forms a non flammable azeotrope with Trans at a ratio 96/4 of Trans/ HFX 110**
- Solstice PF – non flammable**
- HFC 365 – flammable*
- Trans – flammable*

- ** will not ignite
- * will ignite
- FLASH POINT – defined by a specific test

Flammability

- Solstice Propellant – 25%
- Solstice PF - 20%
- Solkane 365 - 15%
- Trans - 35%
- Ethanol 200 proof - 2%
- HFX 110 - 3%
- Low or no flammability

Flammability 2

- Trans - 94%
- Solstice PF - 3%
- DuPont HFX 110 - 3%

- Low or no flammability
- Cost - $3.09/lb.

Flammability 3

- Trans - 95%
- DuPont HFX 110 - 5%

- Non flammable

Regulatory

- Solstice PF – non VOC, GWP < 7
- HFX 110 – non VOC, low GWP**
- HFC 365 – non VOC, GWP 910 *
- HFC 4310 – non VOC, GWP 1300 *
- Trans – VOC, MIR – 1.25

- * Classified by EPA as non VOC, not exempted in California
- ** anticipated to be classified as non VOC

Toxicity

- All solvents have TLVs greater than 200 ppm.