Hair Styling Polymer Review
Value Proposition

Azelis Americas PC and H&IC provides comprehensive service through the delivery of specialty chemical solutions for the formulation of Personal Care and Home Care & Industrial Cleaning products.

Our super-regional footprint accompanied by our technical competence and our optimized marketing platform exemplify our value-added standards to both our supplier partners and customers.
Agenda

• What is a Fixative?
• Polymer Chemistry Overview
• Polymer Properties
• Back of the Deck
  ▪ Formulating Fundamentals
  ▪ Summary
What is a Fixative?

- Are products designed to hold the hair in a desired style for a length of time
- Do not affect the chemical composition or structure of the hair
- Have many forms including aerosol and non-aerosol sprays, mousses, gels, and lotions
- The performance of a styling product is rarely limited to one ingredient. The performance encompasses raw materials, packaging components, and the product form

The key driver is the polymer!
Polymer - Hair Interactions

**Schematic of Hairspray Droplet Impacting Hair**

- Droplet Approaches hair
- Droplet Impacts hair & begins to spread
- Hairspray spreads along adjacent hairs

**Electron Micrograph of Hair to Hair Bond**

- Seam welded

**Extremes of Distribution in Hairspray**

- “Helmet” effect from over wet spray
- Rough “nodule” from over dry spray

**Micro Photograph of Hair to Hair Bond**

- Spot welded
Hard polymers tend to be rather brittle and do not provide strong bonding.
Bond Strength

- Soft polymers are too pliable and ductile to provide effective bonding
Bond Strength

- Polymers which are not too hard, or too soft give the strongest bonds.
The Polymer Choice

• The most important raw material in any styling product is the RESIN. Its main job being to weld or hold the style in place.

• The type of film a hair styling or fixative product forms depends on whether it is used as a styling aid or as a finishing spray.

• The amount of resin used affects the degree of holding power.
  - A higher level of resin forms a harder film and produces a firm hold, while a lower level forms a softer film that is more suitable for a finishing spray.
Polymer Properties and Important Things to Know

• Typical specification may contain
  ▪ Acidity - This is needed to calculate amount of neutralizer needed
  ▪ % solids - Needed to calculate amount of polymer
  ▪ pH
  ▪ % VOC (ethanol)
  ▪ Viscosity
  ▪ K Value

• You typically will not see
  ▪ Tg
  ▪ MW
Polymer Properties and Important Things to Know

- Tg = Glass Transition Temperature
  - Glass transition temperature is a property of amorphous, or semi-crystalline materials.
  - Tg is the temperature at which a polymer starts being able to ‘flow’ ...
    - In crystalline materials Tg does not exist, the melting point take it’s place.
  - Tg does not take account of the added neutralizers and plasticizers
  - Tg does not give an indication of the humidity resistance
  - Tg can be loosely related to hold and flake behaviors
Polymer Properties and Important Things to Know

• Tg = Glass Transition Temperature

- If a polymer’s glass transition temperature is well above (say, 50°C above) ambient room temperature, the material will behave like a brittle glassy polymer - it’ll be stiff with low impact resistance.

- If the Tg is well below room temperature, the material is what is commonly termed a rubber or elastomer and is soft and easily stretch

- If the Tg is reasonably close to the ambient temperature will exhibit plastic material behavior - strong and tough with good impact resistance.
Polymer Properties and Important Things to Know

Molecular Weight

• There are many measures to define the chain length in polymers; each definition depends on the analytical method by which it is measured.

- Gel permeation Chromatography
- Size Exclusion Chromatography

- \( M_w = \) weight average
- Light scattering

- \( M_n = \) number average
- End group titration

- Polydispersity = \( \frac{M_w}{M_n} \)
Polymer Properties and Important Things to Know

• Molecular Weight
  ▪ Assuming similar monomers and conditions, the higher the MW the stiffer the polymer
  ▪ HH conditions will impact stiffness as will monomer selection

• K-Value
  ▪ Measurement of viscosity & flow in a capillary tube
  ▪ Related to MW
  ▪ Longer flow time = higher MW = stiffer polymer
Polymers Properties and Important Things to Know

Acid Value and Neutralization

• Acid value is a measure of the number of acid groups on a polymer molecule.

• Usually, acidic polymers will need to be neutralized for best performance:
  ▪ Improved water solubility
  ▪ Improved ability to be removed from the hair with one shampoo process

• Technical bulletins/websites give the recommended level of neutralization for best performance.

• In manufacturing, as well as in the lab, it is always a good idea to look at the acid value for each lot.
Neutralization

• Generally, hair spray polymers containing carboxylic acid groups need to be neutralized. Neutralization can occur either during preparation of the raw material or while making the aerosol concentrate mixture.

• Neutralization of the acidic groups increases the polymer’s water solubility. This property is key for low VOC formulations that contain substantial amounts of water.

• Polymers containing COOH groups are neutralized to balance shampoo removability with humidity resistance.

• Varying the degree of neutralization affects film stiffness, film clarity, polymer solubility, and propellant tolerance.
Neutralizers

• Un-neutralized or improperly neutralized resins give hard, water resistant films which can NOT be washed easily off the hair.
• The polymer is soluble in ethanol and will go into solution but will not be water soluble if the carboxylic acid groups remain un-neutralized
• Partial neutralization is necessary to make resins removable by shampoo. The degree of neutralization must be balanced to yield good hold (HHCR) and removability.
Neutralizers

• Most common: 2-amino-2-methyl-1-propanol (AMP)

• Other neutralizers:
  ▪ Triisopropanolamine (TIPA)
  ▪ Dimethyl stearamine (DMS)
  ▪ Aminomethyl propanediol (AMPD)
  ▪ Potassium hydroxide (KOH)
  ▪ Sodium hydroxide (NaOH)
Polymer Properties and Important Things to Know

Effects of Increased Neutralization

- Increase shampoo removability
- Increase viscosity
- Increase softness/flexibility
- Increase pH
- Increase corrosion resistance
- Choice of neutralizer can impact performance
- Improve stiffness
  - Use of inorganic bases such as KOH & NaOH
- Improve Hydrocarbon Compatibility
  - Use long chain amines such as DMS
Polymer Properties and Important Things to Know

- Properties of a polymer that will affect hold
  - Molecular Weight
    - Higher MW tends to yield more stiffness
    - Lower MW tends to give better sprayability and lower viscosity
  - Glass Transition Temperature (Tg)
    - Higher Tg tends to be more brittle
    - Lower Tg tends to be more flexible
  - Particle Size (hair spray)
    - Smaller PS can be lower viscosity but also less stiffness
  - Spreadability (gels and creams)
  - Cohesive/Adhesive Balance
  - Hydrophobicity
    - HHCR
  - Ability to form strong spot welds
    - Strength of hold
Polymer Chemistry Overview

• PVP & PVP / VA and various derivatives
• Amphoteric / Anionic - Acrylate Polymers
• Acetate Polymers
• Starch and Cellulose derivatives
• Polyurethanes
• Quats and various derivatives
• PolyVinyl Pyrrolidone (PVP) Chemistry
  ▪ Planar linear molecule with high polarity
  ▪ Non ionic hair fixative, very compatible with carbomer, available in different molecular weights (or K values).
  ▪ The higher the K value the more the ‘crunch’ in the hold characteristics of the polymer
  ▪ Very water soluble via strong H-bonding interactions

<table>
<thead>
<tr>
<th>K value</th>
<th>Mw</th>
<th>Mn</th>
<th>Mv</th>
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<tr>
<td>K90</td>
<td>90</td>
<td>1,200,000</td>
<td>360,000</td>
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</table>
PolyVinyl Pyrrolidone (PVP) Functionality

- Forms hard, glossy, transparent, oxygen permeable, moisture absorbing films
- Solubilizer, binder and dispersant aid
- Stabilizes emulsions and suspensions
- Biologically and physiologically inert

Main Applications

- Styling Gels
- Mousses
- Hair Sprays
PVP + PVP / VA Review

• PVP / VA Copolymers
  ▪ VP (Vinyl Pyrrolidone) is water soluble, VA (Vinyl Acetate) is water insoluble
  ▪ More hydrophobic polymer than PVP, also more flexible. Less tendency to absorb water from the atmosphere
  ▪ Depending on the ratio between the monomers the resulting polymer (a random, linear co-polymer) is water soluble or water insoluble
PVP + PVP / VA Review

Functionality

- **Physical Properties**
  - Aqueous or alcoholic solutions or powder
  - Various ratios of PVP / VA
  - Soluble in water when VP >50

- **Main Applications**
  - Styling Gels
  - Mousses
  - Hair Spray
Additional VP Derivatives

- **VP / DMAEMA (DiMethylAminoEthylMethAcrylate)**
  - (Copolymer 845, 937, 958 from ISP)

- **VP / DMAPMA (DiMethylAminoPropylMethAcrylamide)**
  - (Styleze CC10 from ISP)

- **VP/Methacrylamide/Vinyl Imidazole Copolymer**
  - Luviset Clear AT 3 from BASF
  - Vinyl Caprolactam/PVP/Dimethylaminoethyl Methacrylate Copolymer
    - Advantage LCA from ISP
Summary for VP Family

• PVP & PVP/VA are the market standards
  ▪ Primary polymer for hair gels
  ▪ Cost effective
  ▪ Generally low HHCR
  ▪ The higher the VP & MW - the more stiffness
  ▪ The more VA - the better the humidity resistance, lower solubility
  ▪ Solution & powder forms

• Derivatives designed to improve performance
  ▪ Better spread ability
  ▪ Improved feel
  ▪ Increased HHCR
  ▪ Less “Crunch”
  ▪ More flexible films
Amphoteric / Anionic - Acrylate Polymers

• Traditional technologies used in hair spray
• Contain carboxylate groups that will need neutralization
  ▪ Amphoteric polymer takes on anionic character upon neutralization
• Typical benefits of this class of polymers include:
  ▪ Stiff hold
  ▪ Excellent HHCR
    – Better than PVP
    – Dependant on degree of neutralization and monomer ratio
  ▪ Strong films
  ▪ Good hydrocarbon tolerance

Main Applications:
- Hair Spray
# Amphoteric / Anionic - Acrylate Polymers

## Monomer Type vs. Function

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Function</th>
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</thead>
<tbody>
<tr>
<td>Acrylic Acid</td>
<td>Hydrophobicity, hydrolysis resistance</td>
</tr>
<tr>
<td>(Meth)Acrylic Esters</td>
<td>Adhesion, cationic activity, ionic crosslinking</td>
</tr>
<tr>
<td>t-Octylacrylamide</td>
<td></td>
</tr>
<tr>
<td>Amino Alkyl (Meth) Acrylates</td>
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</tbody>
</table>
Amphoteric / Anionic - Acrylate Polymers

- Acrylate / t-Butylacrylamide Copolymer (Ultrahold Power)
- Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (Amphomer)
- Polyacrylate-22 (Luviset Shape)
- Acrylates Copolymer (Luviflex Soft, Luvimer 100 P)
Acetate Copolymer

- VA/Crotonates/Vinyl Neodecanoate Copolymer
  - Anionic, Carboxylated vinyl acetate terpolymer supplied as a translucent bead
  - Requires neutralization with final pH between 7.5 and 8.5
    - 80 - 90% for initial evaluation Low viscosity and hygroscopic
  - Provides good stiffness
  - Good hydrocarbon tolerance in alcoholic systems
    - A little water may improve tolerance and reduce cloud point
  - Very cost effective workhorse polymer
  - Resyn 28-2930 / Luviset CAN

Main Applications:
- Hairspray
Acetate Copolymer

• VA/Crotonates/Vinyl Neodecanoate Copolymer
  - $X = \text{Vinyl Acetate}$
  - $Y = \text{Crotonic acid}$
  - $Z = \text{Vinyl Neodecanoate}$
# Acetate Copolymer

## Monomer Type vs. Function

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl Acetate</td>
<td>Adhesion, flexibility, low cost</td>
</tr>
<tr>
<td>Crotonic acid</td>
<td>Polarity, adhesion, hydrophilicity</td>
</tr>
<tr>
<td>Vinyl Neodecanoate</td>
<td>Hydrophobicity, hydrolysis resistance</td>
</tr>
</tbody>
</table>
Summary of acrylates and acetates

• Carboxylic acid containing polymers
  ▪ Need to be neutralized
  ▪ Different monomers provide different functions

• Main Application is Hair Spray
  ▪ Provides stiffness and HHCR
  ▪ Strong film formation

• Hydrocarbon tolerance varies from polymer to polymer
  ▪ Supplier literature will provide guidance
Polyurethanes

• Polyurethane-1
  - 100% neutralized, anionic polymer
  - 30% polyurethane, 10% ethanol, 60% water
  - Carboxyl groups already neutralized with AMP
  - MW ~ 10,000 to 15,000 g/mol
  - Very low viscosity at high solids even in 55% VOC formulas
  - No corrosion inhibitors needed
  - Good curl retention
  - Forms flexible yet strong/elastic films
  - Luviset PUR from BASF

Main Applications
- Hair Spray
Polyurethanes

• Polyurethane-14 (and) AMP-Acrylates Copolymer
  ▪ 28% solids with ~ 25% ethanol
  ▪ MW ~ 40,000 daltons
  ▪ No neutralization needed
  ▪ Provides durable, long lasting styles
  ▪ Forms flexible yet strong films for manageability and flexibility
  ▪ Low viscosity at high solids levels
  ▪ Useable in both low and high VOC formulas
  ▪ DynamX from AkzoNobel

Main Applications:
- Hair Spray
- Styling aids
Summary of Polyurethane

- Polyurethanes are newer class of polymers
- Provide more flexible & natural type hold
  - Good HHCR
  - Not as much “Crunch”
- Typically pre-neutralized
- Low viscosity at high solids for better spray aesthetics
- For your long lasting, all day styles
Starch and Cellulose Chemistries

- Naturally derived styling polymers to meet the growing trend for more natural products in the market
- Use various backbone that have been modified to deliver styling benefit
  - Starch
  - Xanthan Gum
- Typically used in styling aids, mousses and gels
Starch and Cellulose Chemistries

• Hydrolyzed Corn Starch (Asensa NFF 11)
  ▪ Modified biopolymer derived from corn starch
  ▪ 99% bio-based, mostly amylopectin starch
  ▪ High degree of branching makes the polymer provide more natural, less stiff hold
  ▪ Water dispersible that forms a latex film on dispersion
  ▪ Off-white powder with low viscosity @ high solids
  ▪ Provides excellent HHCR with a soft feel on hair
  ▪ Helps control frizz
  ▪ Compares favorably to synthetic alternatives

Main Applications
▪ Styling Gels & Creams
▪ Mousse
• **Corn Starch Modified** *(Amaze)*
  - Non-ionic starch fixative modified with propylene oxide
  - Cold water dispersible, off white powder
  - Similar performance profile to synthetics
  - Has low tack on hair and on hand during application
  - Light, clean feel on hair with excellent HHCR
  - Low flaking – especially when combined with different plasticizers
    - Quaternized proteins
    - Glycerin

**Main applications:**
- Mousse
- Gels & Styling aids
Starch and Cellulose Chemistries

• **Dehydroxanthan Gum** *(Amaze XT)*
  - Anionic, naturally derived, multifunctional styling aid
  - Physically modified Xanthan Gum
  - High molecular weight, highly branched molecule
    - mannose, glucose and glucuronic acid
  - Water dispersible with no neutralization needed
  - Off-white powder
  - Provides styling, thickening and suspension in one product
    - Excellent HHCR - long lasting hold
    - High viscosity build at 1 - 2% use levels
    - Low tack with good wet/dry feel

**Main applications:**
- Gels
- Styling Aids
Summary of starch-based technology

• Alternative chemistry to meet natural trend in the market place

• Modified starches can provide good HHCR
  ▪ Good film former
  ▪ Low tack - for soft, touchable hold
  ▪ Primary use in mousse

• Modified Xanthan is multifunctional
  ▪ Styling and viscosity building all in one
  ▪ Primary use in gels for HHCR and stiffer hold
Quat Technology Review

• These technologies provide styling and conditioning benefits
• Cationic in nature provided high level of substantivity
• Forms transparent, flexible films
• Allows for better comb-ability
• Can provide hold, stiffness, HHCR depending on the chemistry
Factors that influence performance of a cationic styling / conditioning polymer

- **Factor**
  - % Nitrogen/charge density
  - Nitrogen Distribution
  - Molecular Weight
  - Amine Type
  - Monomer type

- **Performance**
  - Substantivity, conditioning
  - Surfactant compatibility
  - Viscosity, removability, fixative properties
  - Removability, cationicity vs. pH
  - HHCR, Stiffness, Hold
**Quat Technology Review**

- **Polyquaternium-4** (Celquat L-200)
  - Reaction of DMDAC with ethyl cellulose
  - Comb-like arrangement of nitrogen
  - Various grades providing different levels of hold and conditioning
  - Water soluble and substantive to hair
  - Low flake and excellent HHCR

**Main Applications**
- Mousse
- Hair Gel
• **Polyquaternium-11** (Luviquat PQ-11)
  - Copolymer of vinyl pyrrolidone (VP) and dimethylaminoethyl methacrylate
  - VP provides - Stiffness
  - DMAEMA provides - Flexibility / Combability
  - ~20% solids, ~MW of 1,000,000 daltons, charge density = 0.8 meg/g
  - Provides moderate hold and conditioning
  - Ideal for mousses
Polyquaternium-16 (Luviquat Excellence, Style, etc)

- Copolymer of vinyl pyrrolidone (VP) and quaternised vinylimidizole
- VP provides - Stiffness
- QVI provides - Flexibility, combability, lower MW, higher charge
- Various grades with different MW, charge density and solids
- Provides range of hold and conditioning benefits
- Ideal for mousses and spray products
**Quat Technology Review**

- **Polyquaternium-46** *(Luviquat Hold AT3)*
  - Copolymer of vinylcaprolactam (Vcap), vinylpyrrolidone (VP), and quaternized vinylimidazole
    - Vcap provides - Hydrophobicity, improved HHCR
    - VP provides - Stiffness
    - QVI provides - Flexibility, combability
  - ~ 20% solids, ~ MW of 700,000 daltons, charge density of 0.5 meq/g at pH 7
  - Good hold and HHCR
  - Low charge density makes it ideal for clear hair gels
  - Provides both conditioning and styling benefits

**Main Applications**
- Mousse
- Gel
- Spray
Quat Technology Review

• Polyquaterium-68 (Luviquat Supreme AT1)
  ▪ Copolymer of vinylpyrrolidone (VP), methacrylamide (MAM), vinylimidazole (VI) and quaternized vinylimidazole (QVI)
  ▪ ~20% solids, ~ MW 300,000 daltons
  ▪ Charge density is a function of pH
    - 0.9 meq/g @ pH5 & 0.6 meq/g @ pH 6
  ▪ Excellent HHCR, stiffness and setting ability
  ▪ Low tack and good foam development
  ▪ Water soluble

Main Applications
- Mousse
Quats - Setting vs. Conditioning Performance

- **Setting/ Stiffness**
  - Low
  - Medium
  - High

- **Conditioning**
  - Low
  - Medium
  - High

- **Quats**
  - PQ-16
  - PQ-11, PQ16
  - Anionics plus PQ
  - PQ 46, 55
  - PQ 4, PQ 68,
  - PVP K90
  - VP/Methacrylamide/Vinyl Imidazole Copolymer

Azelis CARE
Quats - Setting vs. Curl Retention Performance

- **VP/Methacrylamide/Vinyl Imidazole Copolymer**
- **PQ 4, PQ 68**
- **VP/VA-Copolymer**
- **PQ 16**
- **PVP K 30**
- **PVP K90**
- **PQ 46, 55**
- **PQ 11, PQ 16**
- **PVP K 30**
- **PVP K90**
Summary

• Fixatives are used to create and set a style

• Many product forms available
  ▪ Hair spray - “finishing” step
  ▪ Mousse - increase body and volume while adding control
  ▪ Gel - provide hold and control

• Polymer choice is critical to creating desired performance
“To Build Unwavering Customer Loyalty”

We accomplish through:

• Developing long-term customer and supplier relationships by providing innovative solutions to meet the formulating and production needs of our customers.

• Employing a leading team of technical sales people, supported by an exceptional service organization.

• Demonstrating the highest level of integrity in every transaction to the mutual benefit of our customers, suppliers and employees.
Back of the Deck
Formulation Tips
Solvent Selection

• What is your VOC target?

• Most commonly used solvents
  ▪ Ethanol
  ▪ Water (non-VOC)

• Alternative solvents
  ▪ Acetone
  ▪ Methyl Acetate
Ethanol

• Benefits
  ▪ Fast drying teams
  ▪ Improved sprayability
  ▪ Polymer solubility

• Limitations
  ▪ Considered a VOC
Solvent Selection

DI Water

• Benefits
  ▪ Non-VOC
  ▪ Can be blended with most other solvents used in hair spray
  ▪ If used alone - can make alcohol free claim
  ▪ Low cost

• Limitations
  ▪ Very slow drying
  ▪ High surface tension
  ▪ Viscosity when blending
Solvent Selection

Acetone

- Benefits
  - Non-VOC
  - Fast dry time
  - Sprayability
  - Polymer solubility

- Limitations
  - Odor
  - Effects on plastic
  - Thought of as “harsh” solvent
  - Label copy
Solvent Selection

Methyl Acetate

• Benefits
  ▪ Non-VOC
  ▪ Fast dry time
  ▪ Sprayability

• Limitations
  ▪ Odor
  ▪ Hydrolysis concerns
Propellants

• A gas under pressure, in a bottle or can, used to expel the contents of the can when the pressure is released (valve is actuated)

• Higher pressure propellants produce finer sprays
• Low pressure propellants give a less forceful spray
• Can be blended to produce appropriate spray aesthetics
• Can also affect polymer solubility
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<tr>
<th>Propellant</th>
<th>Abbreviation</th>
<th>Pressure (psi)</th>
<th>Density (g/cm³)</th>
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<td>Propane</td>
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<td>Dimethy Ether</td>
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<tr>
<td>1,1 Difluoroethane</td>
<td>152A</td>
<td>63</td>
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Additives

• Many types of additives are added for different effects
  ▪ Improve gloss
  ▪ Aid in dry comb
  ▪ Prevent flaking by plasticizing the polymer
  ▪ Improve sprayability
  ▪ Provide UV protection
  ▪ Prevent corrosion
  ▪ Improve flow on hair
  ▪ Label copy
## Additives

<table>
<thead>
<tr>
<th>Additive</th>
<th>Benefit</th>
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<tbody>
<tr>
<td>Cyclomethicone</td>
<td>• Improved sprayability</td>
</tr>
<tr>
<td></td>
<td>• Increased gloss</td>
</tr>
<tr>
<td>Dimethicone Copolyol</td>
<td>• Reduction in surface tension</td>
</tr>
<tr>
<td></td>
<td>• Improved sprayability</td>
</tr>
<tr>
<td></td>
<td>• Reduction in foaming</td>
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</table>
Packaging Components - Pumps

• Particle size: < 100 microns*
• Output: 1.6 ml/stroke or less
• Spray Pattern: 2.5-3”, circular, diffused, break-up in center cone to prevent beading on hair.

*Malvern D[v, 0.5] (median value of particle distribution)
Packaging Components - Valves

• Particle size : 50-90 microns*
• Spray Rate: 0.5 g/sec
• Spray Pattern: 2.5-3”, diffused, reduce/eliminate wet center cone to prevent beading on hair

-VAPOR TAP increase to 0.015 - 0.020” for better particle size break-up in 55% VOC water/DME systems

-Increasing the INNER DIAMETER of the DIP TUBE and decreasing the STEM to increase output while maintaining good particle size

*Malvern D[v, 0.5] (median value of particle distribution)
## Generic Hair Spray Formulas

<table>
<thead>
<tr>
<th>INGREDIENTS</th>
<th>ANHYDROUS</th>
<th>80% VOC</th>
<th>55% VOC</th>
<th>ALCOHOL-FREE</th>
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<tr>
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<td>1993-1999</td>
<td>1999-?</td>
<td>??</td>
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</table>
• The viscosity of an aerosol hair spray concentrate should be kept below 25 cps. (Brookfield, ULA adapter @ 12 rpm).
• The lower the viscosity, the smaller the resultant particle size. However too low, may result in low stiffness and hold on hair.
• The higher the viscosity, the larger the particle size, longer dry times and tack tend to be more perceivable due to the surface tension of the droplet.
• Evacuation over time becomes an issue as the propellant pressure decreases and the work required to push the concentrate up the dip tube increases. This may result in not being able to deliver label claims through the life of the product.
• Pump viscosity should be kept below 15 cps for adequate particle size.
## Low VOC Hair Spray Formulating

### Issues with High Water Content

<table>
<thead>
<tr>
<th>Property</th>
<th>Issue / Measurement</th>
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</thead>
<tbody>
<tr>
<td>Resin Stability</td>
<td>Hydrolysis</td>
</tr>
<tr>
<td>Sprayability</td>
<td>Viscosity</td>
</tr>
<tr>
<td></td>
<td>Surface tension</td>
</tr>
<tr>
<td>Stiffness</td>
<td>Wicking Rate</td>
</tr>
<tr>
<td></td>
<td>Toughness</td>
</tr>
<tr>
<td></td>
<td>Particle Size</td>
</tr>
</tbody>
</table>
## Low VOC Hair Spray Formulating

### Issues with High Water Content

<table>
<thead>
<tr>
<th>Property</th>
<th>Issue / Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial curl droop / Drying time</td>
<td>Water content</td>
</tr>
<tr>
<td></td>
<td>Solvent system</td>
</tr>
<tr>
<td></td>
<td>Viscosity profile</td>
</tr>
<tr>
<td>Can corrosion</td>
<td>Formulation pH</td>
</tr>
</tbody>
</table>
Low VOC Hair Spray Formulating

• **Effects of VOC on Surface Tension**
  - In general - as VOC decreases, surface tension increases
  - Polymer dependant
  - Higher surface tension reduces hold

• **Effects of Wicking Rates**
  - Maximize wicking rate to optimize stiffness
  - Dependant on
    - Viscosity
    - Surface Tension
    - Contact angle
    - Solvent absorption / evaporation

• **Additive to increase wicking rate:** Dioctyl sodium sulfosuccinate
Inorganic neutralization exhibits:

- Significantly greater stiffness/hold
  - Lower formulation viscosity (increases wicking)
  - Less film plasticization

- Improved high humidity curl retention

- Higher formulation pH

*55% VOC, 5% acrylates copolymer, neutralized 100%
Low VOC Hair Spray Formulating

55% VOC Corrosion Inhibition

• **Recommended additives:**
  - Dimethyl oxazolidine
  - MEA-Borate (and) MIPA-Borate

• **Other ways to reduce corrosion:**
  - Be sure to use deionized water to keep anion levels low
  - Increase neutralization to greater than 100% - higher pH helps to prevent corrosion
# Hairspray Troubleshooting

<table>
<thead>
<tr>
<th>Problem</th>
<th>Cause</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poor Shampoo Removability</td>
<td>Polymer is not properly neutralized</td>
<td>• Check percent neutralization calculation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Check acidity of polymer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Check batch card to ensure the proper amount of polymer and neutralizer were added to the batch</td>
</tr>
<tr>
<td>Product does not completely evacuate from the can</td>
<td>Insufficient propellant in the can to evacuate the concentrate</td>
<td>• Carefully evaluate the valve selection. The vapor tap may be too large</td>
</tr>
</tbody>
</table>
# Hairspray Troubleshooting

<table>
<thead>
<tr>
<th>Problem</th>
<th>Cause</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate has precipitate</td>
<td>Polymer may not be soluble in hair spray solvent system alone</td>
<td>• Check order of addition. The neutralizer should be added to the solvent before the polymer.</td>
</tr>
<tr>
<td></td>
<td>Plasticizer or other additives in the formula may not be compatible</td>
<td>• Recheck each additive in the formulation.</td>
</tr>
<tr>
<td></td>
<td>Polymer may not be properly neutralized</td>
<td>• Recheck percent neutralization calculation</td>
</tr>
<tr>
<td>Product won’t actuate</td>
<td>Actuator is clogged</td>
<td>Check actuator for windowing</td>
</tr>
</tbody>
</table>
## Hairspray Troubleshooting

<table>
<thead>
<tr>
<th>Problem</th>
<th>Cause</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray dries too fast</td>
<td>Optimize valve</td>
<td>• Change valving specification</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Change solvent selection</td>
</tr>
<tr>
<td>Spray is too forceful</td>
<td></td>
<td>• Decrease propellant level</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Change valve</td>
</tr>
<tr>
<td>Hairspray needs to have more hold</td>
<td>Polymer level too low</td>
<td>• Increase polymer level</td>
</tr>
</tbody>
</table>
# Hairspray Troubleshooting

<table>
<thead>
<tr>
<th>Problem</th>
<th>Cause</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion</td>
<td>Can formulation incompatibility</td>
<td>• Check concentrate pH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• % Chloride</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Metallic ions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Check source water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Check vacuum</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Check the quality of the can material</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Check to make sure if the can is lined, the lining is compatible</td>
</tr>
</tbody>
</table>
**Styling Gels**

- A thick styling product intended to hold the hair in place while drying, resulting in the desired style and texture
  - Performance dependant on polymer and thickener chosen

- Add shine and give the “wet-look”

- Is expected to stiff, tacky and clear

- Control “fly-aways” and provide long lasting hold while keeping the hair manageable
Styling Gels - Typical Ingredients

- **Thickener**: Acrylate crosspolymer
- **Neutralizer**: AMP
- **Hair Fixative**: PVP, PVP/VA
- **Plasticizer**: propylene glycol, glycerin
- **Chelating agent**: EDTA
- **Additives**: UV Filter, label copy
- **Solvents**: Water, Ethanol
Styling Gels - Typical Polymers

• Non-Ionic
  ▪ PVP, PVP/VA
  ▪ Most common, “crunch” but low HHCR

• Cationic
  ▪ Polyquaternium -4, -11, -16, -44, -68
  ▪ Improved hold and HHCR

• Natural Based
  ▪ Hydrolysed Corn Starch, Corn Starch Modified
  ▪ Good HHCR, “Hand” clarity
## Styling Gels - Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Benefits</th>
<th>Limitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Non-VOC</td>
<td>Slow drying</td>
</tr>
<tr>
<td></td>
<td>Alcohol-free claim</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Non-drying</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low Cost</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polymer solubility</td>
<td></td>
</tr>
<tr>
<td>Alcohol</td>
<td>Polymer solubility</td>
<td>VOC status</td>
</tr>
<tr>
<td></td>
<td>Fast drying</td>
<td></td>
</tr>
</tbody>
</table>
Styling Gels - Thickeners

- **Anionic Polycarboxylate Polymers**
  - Require neutralization
  - Exhibit shear thinning properties
- **Examples**
  - Carbomer
  - Acrylates Copolymer
  - Acrylates/Methacylamide Copolymer
  - Acrylates/Steareth-20 Acrylates Copolymer

- **Naturally Derived Thickeners**
  - Not shear thinning
  - Usually provide slip and detangling as well as thickening
- **Examples**
  - Hydroxyethylcellulose
  - Xanthan Gum
## Styling Gels - Troubleshooting

<table>
<thead>
<tr>
<th>Problem</th>
<th>Cause</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poor clarity or hazy gel</td>
<td>Fisheyes or incomplete hydration of powder</td>
<td>Use different dispersion techniques</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Different mixing blade</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Different mixing speed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Different mixing vessel</td>
</tr>
</tbody>
</table>
# Styling Gels - Troubleshooting

<table>
<thead>
<tr>
<th>Problem</th>
<th>Cause</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decrease in viscosity of carbomer gel</td>
<td>UV light exposure</td>
<td>Add UV absorber</td>
</tr>
<tr>
<td></td>
<td>Transition Metals</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Salt or cations</td>
<td>Use DI water or a chelating agent</td>
</tr>
<tr>
<td></td>
<td>High shear mechanical mixing</td>
<td>Minimize high shear or change to a more stable ingredient</td>
</tr>
</tbody>
</table>
Styling Mousse

• **Mousses are used to:**
  - Provide hold and control
  - Add shine
  - Increase body and volume
  - Improve wet and dry comb
  - Improve wet and dry feel
  - Control “fly-aways”
# Styling Mousse - Typical Formulas

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Aerosol</th>
<th>Non-Aerosol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>1-5%</td>
<td>1-5%</td>
</tr>
<tr>
<td>Water</td>
<td>q.s.</td>
<td>q.s.</td>
</tr>
<tr>
<td>Alcohol</td>
<td>0-15%</td>
<td>0</td>
</tr>
<tr>
<td>Emulsifier/Surfactant</td>
<td>0.5-3.0%</td>
<td>0.5-3.0%</td>
</tr>
<tr>
<td>Other additives</td>
<td>0-2%</td>
<td>0-2%</td>
</tr>
<tr>
<td>Propellant</td>
<td>6-16%</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Styling Mousse - How does it work?

- Concentrate and propellant are 2 separate phases
- Must be shaken immediately before use
- Propellant is emulsified in aqueous phase
- Expansion of propellant when it is expelled from the can produces the foam
- Polymer/emulsifier provides foam stability
### Styling Mousse - Polymer Selection

- Mostly cationic fixative/conditioner polymers used
  - Polyquaternium-68
  - Polquaternium-4
  - Polquaternium-16, -11

- Cationic polymers are substantive to hair

- Provide good wet combing/wet feel properties along with hold
Styling Mousse - Surfactants/Emulsifiers

- Used to aid in foam formation
- Responsible for foam stability
- Mousses should break down quickly when they are worked into the hair
- Commonly used:
  - Isosteareth-10
  - Polysorbate-20, 80
  - Oleth-20
  - Laureth-23
  - Sodium cocoyle isethionate
  - PEG-6 cocamide
Styling Mousse - Propellants

- Propellant A-46 most commonly used

- Other propellant blends may be used to achieve desired foam properties

- Blends of hydrocarbon propellants and propellant 152A can be used to increase overall propellant level without violating VOC restrictions
# Styling Mousse - Troubleshooting

<table>
<thead>
<tr>
<th>Foam density does not match benchmark</th>
<th>Surfactant level or type may not be correct</th>
<th>Propellant pressure may be incorrect</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• Alter surfactant</td>
<td>• Alter surfactant</td>
</tr>
<tr>
<td></td>
<td>• Change surfactant level</td>
<td>• Change propellant</td>
</tr>
</tbody>
</table>


Evaluations
Common Test Methods

- HHCR - 8 to 24 hr, 90% humidity, RT
- Half Head Test - lab and salon comparisons
- Three point bend test - for stiffness of polymers
- Wet and Dry comb on Diastron - for conditioning benefits
- Flake evaluation of tresses and half-heads
- Standard subjectives on tresses
- Microscopy and for hair damage
- Salon and consumer evaluations
# Polymer Properties and Important Things to Know

- Examples of $T_g$ at 0% R.H. for different polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
<th>Notes</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP K 30</td>
<td>175</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VP/ VA 73</td>
<td>115</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VP/ VA 64</td>
<td>106</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VP/ VA 55</td>
<td>89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VP/ VA 37</td>
<td>66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VP/ VA 28</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylates copolymer (acidic)</td>
<td>80</td>
<td>(needs neutralization for best performance)</td>
<td></td>
</tr>
<tr>
<td>Acrylates copolymer (100% neutralized with AMP)</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyurethane-1 (pre-neutralized with AMP)</td>
<td>-7 C  + 57 C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Polymer Properties and Important Things to Know

Neutralizers

Neutralization pH change
Polymer Properties and Important Things to Know

Weight of neutralizer needed, (g) = $A \times B \times C \times D$

$1000$

$A = \text{weight of polymer (g)}$

$B = \text{equivalent weight of neutralizer (g/eq)}$

$C = \% \text{neutralization desired (decimal)}$

$D = \text{acidity of polymer (meq/g) - measures amount of acid groups}$

*Begin by using neutralization levels recommended by the manufacturer*
PVP + PVP / VA Review

- Increasing the proportion of VA reduces the water absorption
Additional VP Derivatives

• VP / DMAEMA (DiMethylAminoEthylMethAcrylate)
  ▪ (Copolymer 845, 937, 958 from ISP)
  ▪ Copolymer that is pseudo-cationic and substantive to negatively charged surfaces
  ▪ Forms transparent, flexible glossy films
  ▪ Provides hold, gloss, manageability and smooth feel to hair
  ▪ Improves spreadability
  ▪ Soluble in ethanol & water
  ▪ Compatible with nonionic, cationic and amphoteric surfactants

Main Applications
▪ Gels
▪ Mousses
▪ Pomades
Additional VP Derivatives

- VP / DMAPMA (DiMethylAminoPropylMethAcrylamide)
  - (Styleze CC10 from ISP)
  - Copolymer that is pseudo-cationic and substantive to negatively charged surfaces
  - Forms transparent, flexible glossy films
  - Provides hold, gloss, manageability and smooth feel to hair
  - Improves spreadability
  - Soluble in ethanol & water
  - Compatible with nonionic thickeners and various surfactants

Main Applications
- Gels
- Mousses
- Pomades
Additional VP Derivatives

• VP/Methacrylamide/Vinyl Imidazole Copolymer
  ▪ Luviset Clear AT 3 from BASF
  ▪ Water soluble, non-ionic hair setting polymer
  ▪ Strong hold, low tack, fast drying
  ▪ Provides excellent resistance to high humidity and thermal protection
  ▪ Can make crystal clear gels with carbomer
  ▪ 20% solution

Main Applications
▪ Gels
▪ Mousses
▪ Pump sprays
Additional VP Derivatives

• Vinyl Caprolactum Polymers
  ▪ Vinyl Caprolactam/PVP/Dimethylaminoethyl Methacrylate Copolymer
    - Excellent hydrocarbon tolerance
    - Good HHCR
    - Low formulation viscosity
    - Use in low to high VOC HS
    - Yields flexible hold
    - Advantage LCA from ISP
Polyvinylcaprolactam (PVCap) versus Polyvinylpyrrolidinon (PVP)

- Polarity shift and Tg shift transform Polyvinylcaprolactam from humidity sensitive to humidity proof
- High Curl Retention compared to PVP
Amphoteric / Anionic - Acrylate Polymers

- **Acrylate / t-Butylacrylamide Copolymer** *(Ultrahold Power)*
  - 30% solution in Ethanol
  - Needs to be neutralized: 80 to 100% with AMP
  - Final pH should be between 8.0 - 9.0
  - Forms a clear, hard non-tacky film
  - Excellent setting properties with noticeable stiffness and curl retention under humid conditions
  - Delivers enhanced shine
  - Compatible with other styling polymers
  - Good for low and high VOC formulas
  - Pump and aerosol hair sprays
Amphoteric / Anionic - Acrylate Polymers

• Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer (Amphomer)
  - Off white powder soluble in alcohol & aqueous alkali
  - Needs to be neutralized: 80 to 100% with AMP
  - Final pH should be between 8.0 - 9.0
  - Forms a clear, hard non-tacky film
  - Very stiff feel and excellent HHCR
  - Various grades using different monomer ratios to alter performance
  - Plasticizers often used to improve gloss and feel on hair
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer

\[
\begin{align*}
\text{a} & : \text{COOR}_1 \\
& \quad \text{H}_2\text{C}-\text{C}- \\
& \quad \quad \text{CH}_3 \\
\text{b} & : \text{COOH} \\
& \quad \text{H}_2\text{C}-\text{CH}- \\
\text{c} & : \text{C}\left(\text{CH}_3\right)_3 \\
& \quad \text{NH} \\
& \quad \text{C}=\text{O} \\
& \quad \text{H}_2\text{C}-\text{CH}- \\
\text{d} & : \text{COOR}_2 \\
& \quad \text{H}_2\text{C}-\text{C}- \\
& \quad \quad \text{CH}_3 \\
\text{e} & : \text{CH}_3 \\
& \quad \text{O}=\text{C}\cdot\text{O}\left(\text{CH}_2\right)_2\text{NHC}\left(\text{CH}_3\right)_3 \\
\end{align*}
\]

\[R_1 = \text{alkyl and } R_2 = (\text{hydroxy})\text{alkyl}\]
Amphoteric / Anionic - Acrylate Polymers

- **Polyacrylate-22** *(Luviset Shape)*
  - Copolymer of methyl methacrylate, methacrylic acid, acrylic acid and urethane acrylate
  - Partially neutralized (~60%), anionic polymer soluble in ethanol, water and mixtures @ pH 6.0 - 9.0
  - Solution polymer with ~ 34% solids
  - Very high Tg ~ 125 - 135 C with MW ~ 35,000 to 50,000 daltons
  - Crunchy, stiff hold
  - Long lasting hold and HHCR
  - Fast drying with low tack, low foam and flaking
  - Neutralization to adjust from crunchy to flexible hold
  - Ideal for low VOC systems
Amphoteric / Anionic - Acrylate Polymers

• **Acrylates Copolymer** *(Luviflex Soft, Luvimer 100 P)*

  • **Terpolymer of tert-butyl acrylate, ethyl acrylate and methacrylic acid**
    - Many grades available
      - Powders for anhydrous to high VOC
      - Emulsion polymers for low VOC
      - Certain grades designed to be corrosion resistant
    - Anionic when neutralized
    - Good hydrocarbon tolerance
    - Gives strong hold with good curl retention

**Main Applications:**
- Hair Spray
- Styling Aids
Amphoteric / Anionic - Acrylate Polymers

• Acrylates Copolymer (Luviflex Soft, Luvimer 100 P)
  - Terpolymer of tert-butyl acrylate, ethyl acrylate and methacrylic acid

\[\text{CH}_3\] \text{O} \backslash \text{COR} \quad \text{CH}_3 \backslash \text{CH}_2\text{-C-} \quad \text{H} \backslash \text{COR} \quad \text{CH}_3 \backslash \text{CH}_2\text{-C-} \quad \text{COH} \]
Effect of Polymer Composition

Aerosol Cloud Point

Shampoo Removeability

| System: 2% polymer, 90% neutralized with AMP, 35% isobutane/propane (80/20), balance SDA-40 |

<table>
<thead>
<tr>
<th>% Vinyl Acetate</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Crotonic Acid</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>% Vinyl Neodecanoate</td>
<td>---</td>
<td>15</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

Removability Rating: 1 1 2 4

Rating Scale

Completely Removable

Not Removable

10/17/17