Society of Cosmetic Chemists
California Chapter

Understanding What Can Go Wrong With Cosmetics & Personal Care Products

IFC SOLUTIONS
Blending and Ingredient Specialists Since 1939

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What this presentation will cover:

1- Cosmetic Ingredients
2- Cosmetic Emulsion Types
3- Cosmetic Product Testing
1 Basic Ingredients used in Cosmetics
Types of Cosmetic Products

There are 10 basic categories of cosmetic formulations. These include:

- Solutions
- Gels
- Creams / Lotions
- Tablets
- Other Emulsion Types
- Powders
- Ointments / Pastes
- Sticks
- Suspensions
- Aerosols
The Troubleshooting Process

Identifying Basic Ingredient Differences

Understanding ingredient parameters can be an indicator of differences and potential problems with a formulation.

Be familiar with ingredient specifications (odor, color, appearance, feel, application, texture, etc.)
Also understand each ingredient’s C of A.

One must understand the relationship and interactions ingredients have with other ingredients.
In order to troubleshoot problems quickly and effectively, it is important to understand cosmetic ingredients and how they are used in formulations as well as their processing capabilities and limitations.
Cosmetic Ingredients

Classifying Emollients

EMOLLIENTS (AND SOLVENTS)

NON-POLAR
- PARAFFIN MINERAL OIL
- ISO-PARAFFIN HYDROCARBONS

POLAR
- WAXES, ESTERS & VEGETABLE OILS
- GLYCERIDES
  - Mono
  - Di
  - Tri
- STRAIGHT-CHAIN
- BRANCHED-CHAIN
- SATURATED & UNSATURATED

MINERAL WAXES

PETROLATUM
POLAR versus NON-POLAR

A solvent’s polarity is determined by its dielectric constant which is a solvent’s ability to reduce the field strength of the electric field surrounding the charged particles immersed in it.

A dielectric constant of greater than 15 indicates that a solvent is polar.
A dielectric constant of less than 15 indicates non-polarity.

Polar ingredients easily dissolve other polar ingredients. The same is true for non-polar ingredients.

Polar ingredients mix poorly with non-polar ingredients; Must use co-solubilizers that have compatibility with both.
Emollients and Occlusivity

<table>
<thead>
<tr>
<th>Emollient</th>
<th>Occlusivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrolatum</td>
<td>98%</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>62%</td>
</tr>
<tr>
<td>Glyceryl Triisostearate</td>
<td>47%</td>
</tr>
<tr>
<td>Propylene Glycol Diisostearate</td>
<td>27%</td>
</tr>
<tr>
<td>Propylene Glycol Monoisostearate</td>
<td>15%</td>
</tr>
</tbody>
</table>

Occlusivity of Isostearate Esters increases almost linearly with the increase in Molecular Weight.

Moisturization is a result of occlusivity and a reduction in **TEWL**.
Trans Epidermal Water Loss

To Improve Moisturization

You can’t add moisture to the skin but you can prevent moisture from leaving.
Trans Epidermal Water Loss

Must Improve Barrier

Create an Occlusive Film

Emulsion or Other Film Type
Spreadability increases with polarity, lower molecular weight and degree of branching.
Silicones in Cosmetics

Solubility Characteristics of 3 Common Silicones

<table>
<thead>
<tr>
<th>Material</th>
<th>100 cst Dimethicone</th>
<th>Cyclomethicone</th>
<th>Phenyltrimethicone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>NS</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>NS</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Water</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>IPP</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>IPM</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Mineral oil</td>
<td>NS</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Beeswax</td>
<td>NS</td>
<td>SH</td>
<td>SH</td>
</tr>
<tr>
<td>Carnauba wax</td>
<td>NS</td>
<td>SH</td>
<td>SH</td>
</tr>
<tr>
<td>Aromatic solvents</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Aliphatic solvents</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Octylmethoxycinnamate</td>
<td>PS</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Octyl salicylate</td>
<td>NS</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Lanolin</td>
<td>NS</td>
<td>SH</td>
<td>SH</td>
</tr>
</tbody>
</table>

S = soluble; NS = not soluble; PS = partially soluble; SH = soluble hot.

This information can determine what type of cosmetic system silicones will work best in. Solubility limits are available from most suppliers.

Volatile silicones can be either cyclic or low viscosity linear dimethicones.

Silicone polymers enhance water resistance.
Gums & Thickeners
For Foundations and Emulsions to Control Rheology

Veegum
(Magnesium Aluminum Silicate)

Carboxy Methyl Cellulose (& other Cellulosic Gums)
Xanthan Gum  Carageenan  Guar Gum

Carbopols  Silicas

Clays and Organomodified Clays

Synthetic Polymeric Materials
(Acrylates & Urethanes)
Understand your Ingredient “TEAM”

• Not all ingredients play well together in a particular cosmetic system.

• Some ingredients are weak in certain systems due to incompatibility or solubility but are necessary to provide specific form and function.

• These ingredients must be held in the system by stronger more compatible ingredients in order to stabilize the formula.

• A formulator must understand each ingredient’s inherent strengths and weaknesses in specific cosmetic applications.

• The use of co-solvents and co-solubilizers must be used to overcome and balance out these strengths and weaknesses.

• This makes for a very cohesive “Team” of ingredients that will result in a stable functional formulation.

• Ingredient “Teams” may vary depending on the type of cosmetic product.
2

Cosmetic Emulsion Types
Types of Emulsions

Most Common Emulsion Types

O/W
Oil-in-Water

W/O
Water-in-Oil
Oil-in-Water

Water is external or continuous phase. Pigments are ground into the external phase and oil (the internal or discontinuous phase) is added to the water phase.
Water-in-Oil

Oil is the external (continuous) phase. Pigments are ground into the oil phase and water phase is added to the oil phase.
Emulsions

Emulsions can be the most difficult cosmetic products to formulate. To guarantee the repeatability of an emulsion, the rate of phase addition in any batch size should be constant.

In oil-in-water type emulsions the oil phase is added to the water phase at a sufficient emulsification temperature (70-75º C).
Water should be the larger and external (continuous) phase.

Water-in-oil emulsions require less heat (60-65º C) but more energy and sheer is necessary to form the emulsion. The water (internal) phase is added to the oil (external) phase. Phase ratio and rate of addition are critical.
Emulsions

Most common formulas are examples of anionic (oil-in-water) emulsions composed mainly of a **TEA-Stearate** soap system. These emulsions require a neutralization reaction.

The **pH** of a properly neutralized TEA-Stearate emulsion should be **8.0 - 8.4**. Water-in-Oil emulsions usually do not have a measurable pH since water is the internal phase and surrounded by the oil phase. They are also non-conductive.

This is where **HLB** becomes very important. Nonionic emulsions contain no soap system. (But can contain ethoxylated emulsifiers and co-emulsifiers) An emulsion’s pH can be to the slightly acidic side to help deter microbial growth and enhance its preservative system.
Every ingredient has an HLB value assigned to it. This number is called a required HLB.

Oil soluble (Lipophilic) ingredients have a low HLB. Water soluble (Hydrophilic) ingredients have a high HLB.

To combine the water soluble ingredients and water soluble ingredients, a combination of low HLB and high HLB emulsifiers must be used.

Each emulsifier has an affinity for either water or oil.

Oil soluble emulsifiers have a water loving area that attaches to the water phase; Water soluble emulsifiers have an oil loving end that attaches to the oil phase.
A Product must be stable at all temperatures & conditions. There should be **no** separation, sweating or color bleed.

\[
\text{HLB} = \text{Hydrophobic/ Lipophilic Balance} \\
[ \text{Low HLB} = \text{Oil loving} / \text{High HLB} = \text{Water loving} ]
\]

A balance must be achieved between water loving and oil loving materials to ensure product stability with the help of emulsifiers.

\[
\text{HLB} = \frac{(\text{Amount of 1st emulsifier})(\text{HLB of 1st emulsifier}) + (\text{Amount of 2nd emulsifier})(\text{HLB of 2nd emulsifier})}{(\text{Amount of 1st emulsifier} + \text{Amount of 2nd emulsifier})}
\]

**Viscosity Control**

Must have good rheological properties - should not build in viscosity over time. A liquid must continue to flow even when aged.

**Color Fading**

Colors must be placed in proper phase and must not migrate. Colors migrating to internal phase (discontinuous phase) will fade. Color should not fade over time.
Emulsifiers are designed to attach themselves to the part of the molecule they have an affinity for and keep the two unlike phases from coming apart.

Emulsifiers come in many different types and chemical families. Some work better than others depending on the ingredients and type of emulsion.

Stearate-based emulsifiers may work well in one system while oleate-based emulsifiers work best in others.

The fatty acid end of a molecule must be chosen carefully as many different emulsifiers can have the same HLB but not all will work the same or successfully in every system.
HLB

A properly neutralized Fatty Acid-Alkali soap system should have a mid-range HLB value of 7.00 as with TEA-Stearate emulsions.

With the advent of new molecules, specialty chemicals, polymers, and silicone chemistry - the HLB system is becoming more and more difficult to work with and calculate.

Some ingredients have great difficulty being stabilized as they sometimes lack having a required HLB value assigned to them. This makes it difficult to calculate the HLB of the entire emulsion system to determine the proper emulsifiers to use.

As more ingredients are added, the HLB balance changes and additional surfactants or co-emulsifiers may be needed. This may require a large amount of trial and error.
HLB of Emulsifiers

These values are approximate and are formula-dependent.
HLB of Emulsifiers

Example of an HLB Value Calculation

Oleth-20 is a 20 mole Ethoxylate of Oleyl Alcohol (also called BRIJ 98)

We calculate the molecular weight of the 20 moles of Ethylene Oxide (one mole ETO = 44) \(20 \times 44 = 880\)

We add this number to the molecular weight of the Oleyl Alcohol \(880 + 270 = 1150\) (the molecular weight of BRIJ 98)

What percentage of 1150 is 880 ?
\[
\frac{880}{1150} = 76.5\%
\]

76.5% divided by \(5 = 15.3\)

The HLB Value for Oleth-20 is 15.3
Appearance of Emulsions

The appearance of the emulsion is related to the size of the particles or droplets which are dispersed or suspended in the external phase:

- **Opaque White**: > 1 micron particle size
- **Bluish White**: 0.1 to 1 micron particle size
- **Opalescent**: 0.05 to 0.10 micron particle size
- **Transparent**: < 0.05 micron particle size
Emulsion Stability is dependent on many factors:

- Proper temperatures during emulsification
- Phase ratio and proper phase addition
- Percent of powder fill
- Particle or droplet size and shape
- Rate of phase incorporation (Speed of phase addition)
- Improper manufacturing or filling equipment
- Adequate emulsification system & Sufficient emulsifiers
- Proper HLB of System
- Incorporation of Air
- Heating and Cooling Rates
- Temperature during Filling, Storage & Transit
- Microbiology
Pigment Processing

As supplied, pigments are highly agglomerated and sometimes aggregated. Particle size can be as high as 100 microns or more. Optimum particle size should be 3µm to 5µm. The proper grinding equipment must be used to guarantee particle reduction.

Primary Particle

Aggregate - Tightly Bound

Agglomerate - Loosely Associated
Product Separation

Incorrect Phase Addition or Phase Ratio Off

Wrong Emulsifier Choice or Inadequate Levels of Emulsifiers

Incorrect HLB

Unground or Poorly Ground Pigments

Improper wetting of gums and thickeners

Low Zeta Potential
Zeta Potential

Zeta potential is the difference in electrical potential between the dispersed medium and the stationary layer of fluid attached to a dispersed particle or droplet.

Zeta potential which is measured in milliVolts (mV) is the charge that develops at the interface between a material’s surface and the liquid medium it is dispersed in.

A zeta potential of ~25 mV is said to be the borderline value to determine if an emulsion will remain stable.

The significance of zeta potential is that its value can be related to the stability of colloidal dispersions and emulsions.

The zeta potential indicates the degree of attraction or repulsion between adjacent, similarly charged particles, such as droplets, pigments and dry powder fillers, in dispersions and similar colloidal systems.
Zeta Potential

Zeta Potential can be affected by the following factors:

pH – Acid / Base Ratio

Electrolyte / Salt Levels

Conductivity

Concentration of critical components in a Formulation
Zeta Potential

When the potential is low, particle attraction exceeds repulsion and the dispersion will break, flocculate and separate (see chart below).

Dispersions with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to separate.

*Increasing* the zeta potential *Improves* an emulsion’s stability.

Zeta potential can be regulated or altered using salts which at high levels will reduce the electrical potential, or by coating the particles with polymers or surface treatments thereby causing steric repulsion where van der Waals forces are too weak to cause the particles to adhere to one another.

<table>
<thead>
<tr>
<th>Zeta Potential (mV)</th>
<th>Stability Behavior of the Colloid</th>
</tr>
</thead>
<tbody>
<tr>
<td>from 0 to ±5</td>
<td>Rapid coagulation or flocculation</td>
</tr>
<tr>
<td>from ±10 to ±30</td>
<td>Some instability</td>
</tr>
<tr>
<td>from ±30 to ±40</td>
<td>Moderate stability</td>
</tr>
<tr>
<td>from ±40 to ±60</td>
<td>Good stability</td>
</tr>
<tr>
<td>more than ±61</td>
<td>Excellent stability</td>
</tr>
</tbody>
</table>
Product Separation

Typical flocculation in an emulsion as seen magnified through a microscope.

This is when droplets separate and aggregate into larger groups becoming heavier and settling out.
Process Development and Product Scaleup

Manufacturing - This is where things can really go wrong.
Process Development and Scale-Up
Chain of Events

Product Concept
Laboratory Development
Pilot Batches for Process Optimization
Filling Trial / Test Fill
Line Trial
Purchasing of Raw Materials and Packaging Components
Manufacturing Direction
Pre-Production Batches
Production / Manufacturing / Full Scale-Up
Product Filling / Packaging / Distribution to Counter
Product Scaleup

Lab development must never be performed using equipment or processes that do not exist, are the incorrect size, or not reproducible in production:

- Oversized Homogenizer Heads
- Oversized Props
- Excess Mixer Speeds
- Non-Repeateable Mixing Techniques
- Makeshift Tools
- Hand Pouring versus Pump Speeds
- Horsepower Equivalencies
Product Scaleup

Phase additions must be the same (oil into water or water into oil) regardless of batch size.

Example: The time it takes to add an oil phase to emulsify a 1 Kg batch should be the same as when you add that same oil phase to a 1000 Kg batch.

From 1 Kg to 1000 Kg, horsepower, rpm’s, prop size and shape, or other mechanical or kinetic attributes must be scaled up or calculated accordingly.
Product Scaleup

If these constants are not met, the resulting product can be different in feel, application, texture, viscosity, drydown, and even color.

It can even change the specific gravity or other physical attributes.

Can’t meet fill weight or product drips or won’t pour.

It may affect the product’s stability, claims, OTC and laboratory test results or other critical parameters.
Product Scaleup

Try not to change ingredient lots or suppliers from lab to production unless verified first that they are equal.

Scaleup from lab to manufacturing is critical.

The equipment and mechanics may not be the same.

The following slides show the comparison of equipment used in the lab and how it compares with equipment used in manufacturing.
Scaleup Issues

What problems may occur while going from laboratory to production?

How can they be avoided?
Scaleup Issues

Problems in production can be caused by equipment issues

While other issues can be traced back to ingredients or suppliers

Troubleshooting in production can either be simple or difficult

Partner with your process engineer during the development process
The Process Engineer

The Brains behind the Big Batch

Knows equipment and processing

Understands the physics behind product manufacturing

Creates proper procedures for any batch size and helps reproduce any product in any quantity the same way every time

Can help troubleshoot problems
3

Product Testing
Stability & Product Testing

- Product-Specific Laboratory Stability
- Package Testing
- Microbiology Challenge Testing
- Safety Testing
- Sensory Testing
- OTC Drug Testing
- Other Testing
- Color Evaluation
The Package Specifications used in the lab to develop a formula must be the same as the specifications used in full-scale manufacturing.

If the specifications do not match or are too wide then the product will not have the same performance features.

Package/Product compatibility must be tested well in advance.

Package in-use can trap moisture which can lead to micro issues.

Airtight package must be airtight.
Laboratory Stability

Basic Testing Based on Product Type:

• Viscosity / Rheology
• pH
• Elevated Temperature Stability:
  25°C (R/T control), 37°C, 45°C, [50°C (rarely used - too extreme)]
• Freeze-Thaw (2 cycles minimum, to - 4°C)
• Melt Point / Hardness (Degrees Celsius - ºC)
• Solids Content (110°C for 2 hours)
• % Water (Karl Fischer Titration)
• Specific Gravity / Bulk Density (grams/cc or in³):
  For package fill weight determination & verification
• Package Testing & Compatibility
• Microbiology - Challenge Tests & Plate Count
• Centrifuge (@ 3000 rpm)
Viscosity

Viscosity is the measure of the internal friction or resistance to flow of a material or fluid. Friction is usually a function of a material’s thickness.

Rheology is the study of the changes in flow characteristics of a material or fluid.

All materials have a tendency to flow no matter how thick they are.

Newtonian fluids are those that at any given temperature will have no change in viscosity, and the viscosity will remain constant no matter how much shear or stress is applied.

Examples: water, ethanol, cyclomethicones and thin motor lubricating oils
• Viscosity $\eta$ measured in poise or centipoise

• Shear Stress $F$ measured in dynes/cm$^2$
  Force per unit area required to produce a shearing action.

• Shear Rate $S$ measured in sec$^{-1}$ (or reciprocal seconds)
  Measure of the rate of change in speed at which layers move past one another and exhibit a shearing action.

• Different viscometer spindle geometries require different equations and calculations (time/speed factors).
Viscosity is measured in **poise** - A material requiring a shear stress of 1 dyne per square centimeter to produce a shear rate of 1 reciprocal second has a viscosity of 1 poise or 100 centipoise *(Metric Measure)*

\[10 \text{ poise} = 1 \text{ Pascal-second} \quad \text{and} \quad 1 \text{ centipoise} = 1 \text{ milli-Pascal-second} \quad \text{(International Measure)}\]

**Thixotropy** - Viscosity will thin down when a force or stress is applied. With time, the original viscosity will recover until additional forces or stresses are re-applied.
Microbiology

Natural & Synthetic Preservatives

Broad Spectrum Preservatives should be used to kill Bacteria, Mold & Yeast

Over 60 different Preservatives are approved for use in cosmetics in the United States

The use of “Non-Preservative” Preservatives is becoming very popular
Microbiology

Challenge Test
A test conducted on a cosmetic sample to determine if its preservative system will kill a selection of the most common microorganisms even several after re-inoculations over a 12-week period. There should be no growth.

Plate Count
This test determines if there are any microorganisms present in a particular test sample. Usually done on every newly manufactured batches prior to filling and distribution.

Preservative Effectiveness Test (PET)
This test determines if the preservatives in a particular cosmetic system are adequate and effective at protecting the product from microbial growth. This test is based on a single plating of microbiological media which has been previously validated for the most commonly used preservative systems.
Microbiology

Since an Emulsion contains water it must be adequately preserved and pass a full 12-week micro challenge test. Everyone uses the same pool of microorganisms to run challenge tests. A product must never be over-preserved. Products must be protected from consumer contamination.

Anhydrous products - lipsticks & hot pours contain no water and do not support microbial growth. It is too hostile an environment for microorganisms to grow.

Honey - Self-Preserving - - - - Based on Water Activity

Products can be filled and micro tested in their proper / final package.
Microbiology

**Water Activity**

Water Activity $A_w = \frac{\text{Vapor Pressure of Formula}}{\text{Vapor Pressure of Water at Same Temperature}}$

Water activity (amount of free water) can determine the ability of microorganisms to grow in a certain cosmetic system and how much of a preservative system may be required.

Preservatives will work better if the formula is on the acidic side (low pH) and if additional ingredients are added to enhance their activity.
pH and Microbial Growth

Optimum pH for Microbial Growth

- Bacteria: pH between 5.5 and 8.5
- Fungi (Yeast and Mold): pH between 4.0 and 6.0

Note: Most microorganisms will grow between pH 4.0 and 9.0

There are some microbial species that can grow at a pH above and below this range.

Some microbial species are even preservative resistant.
Preservation versus Extended Shelf Life

There are some misconceptions about antioxidants being called preservatives:

Preservatives KILL microorganisms

Antioxidants INHIBIT the growth of microorganisms (but do not kill) therefore they can prolong shelf life.
Ingredients that enhance preservative activity but are not preservatives:

- **Glycols:**
  - Propylene Glycol
  - Butylene Glycol
  - Hexylene Glycol
  - Zemea® (1,3 Propanediol)

- **Various Esters:**
  - Caprates
  - Caprylates
  - Ethylhexylglycerin (Sensiva SC50)

- **Antioxidants:**
  - Vitamin E, C, E
  - BHT, BHA
  - Coenzyme Q10
  - Lycopene
  - Natural Extracts & Essential Oils*

*Essential Oils - Many have varied degrees of “antimicrobial activity”

Preservative Deactivators: Cellulose; Lecithins; Polysorbates
Microbiology Issues

Cosmetics can also have microbiology issues if:

- Preservatives are highly temperature sensitive
- Added to the wrong phase or poorly solubilized
- Preservatives can be deactivated due to other ingredients in the formula
- Are added to a phase at the wrong pH especially if the preservatives work only within a specific pH range.
For most cosmetic products, the government agencies such as the Food and Drug Administration in the U.S., COLIPA in the EU, and JCIA in Japan, require minimum testing to be conducted on new products prior to being marketed to consumers to determine their safety.

There are number of basic clinical tests that are considered the minimum required in order to determine the safety of a cosmetic product.

The government leaves it to us to guarantee that the products we put on the market are safe and will not harm the consumer.
So Why Clinical Testing ??

If a product is *not* tested, it must be labeled as such (21 CFR Section 740.10):

“Warning - The safety of this product has not been determined”

> RIPT (Human Repeat Insult Patch Test)
  100 panelists

> In-vitro Ocular (for eye products)
  To determine if a eye product causes eye irritation

> Micro Challenge Test / PET
  12 weeks with re-innocation / Plate counts on production batches
  Microbiologists look for a log\(_{10}\) reduction in microbial counts.
But Why Clinical Testing ???

To make sure your product does not do this:

To avoid product irritation leading to consumer complaints and returns, or worse.
CONCLUSIONS

• A formulator must be familiar with all the cosmetic ingredients and raw material suppliers used in any color or cosmetic formulation.

• A formulator must know how to manufacture various color cosmetic products and be familiar with the way the go and don’t go together.

• A formulator must know what equipment to use to manufacture the various types of color cosmetic products.

• A formulator must know how to test all the various cosmetic products and to understand the results of these tests, what they mean and how to evaluate and utilize all the data from these tests.
CONCLUSIONS

• It is much simpler to troubleshoot a formula that contains fewer ingredients as it will be easier to locate the suspected ingredient or process that is causing a particular problem.

• It is sometimes more difficult to reproduce a mistake when you’re trying to solve a specific problem.

• Mistakes are o.k. - it shows what not to do the next time but they may also be an indicator of where a problem may lie.

• You can never learn anything if you don’t make mistakes.
CONCLUSIONS

• Look for the obvious - then the not so obvious. Be creative in your thinking - always expect the unexpected.

• Problems should be solved before they get to the cosmetics counter.

• Always remember what you’ve learned - you never know when you’ll need it again or when you’ll have to teach it.

• Take note of all the new techniques you develop and document everything in your lab notebook.

• Good luck with your problem solving.