# Unit 3
# Formulation Building blocks:

Lipstick

Nail Polishes



Perfumes

Eye shadows


Soaps

Deodorants


Creams

Shampoos

Antiperspirants

Toothpastes

# Cosmetic Ingredients

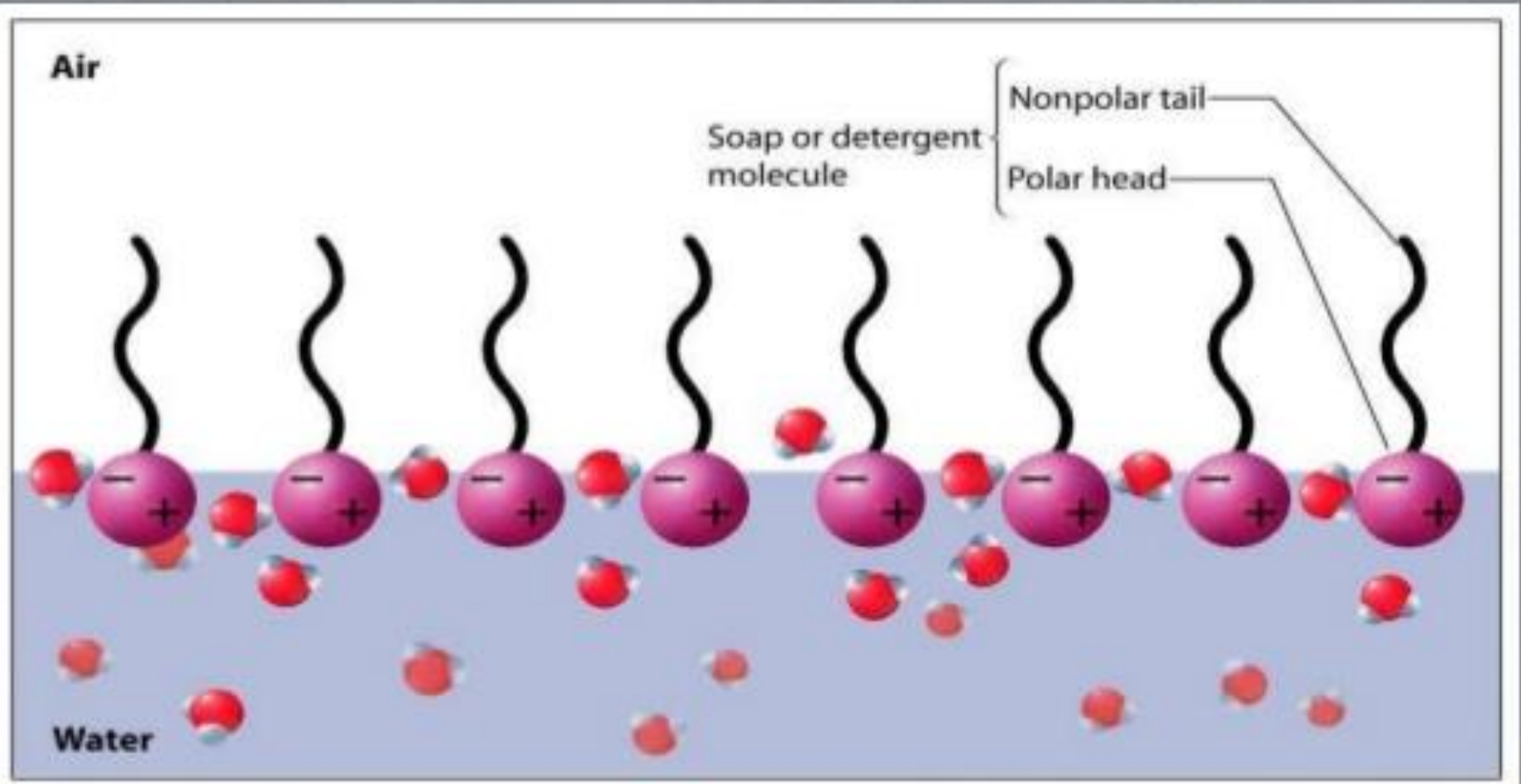
- Abrasives
- Stain remover
- Moisturizers
- Emollients
- Propllents
- Surfactants
- Antioxidants
- Plasticizers
- Preservatives
- Thickeners
- Solvents
- Sweeteners
- Chelating Agents
- Flavouring Agents
- Fragrance
- pH buffers
- Occlusive Agents
- Dye/Pigments/Lake

# Surfactants
# Classification and application

# Surfactant

- Surfactants are usually organic compounds that are amphipathic, that is they contain both non-polar or hydrophobic groups (their ‘tails’), typically a long alkyl chain, and polar or hydrophilic groups (their ‘heads’).
- Therefore, they are soluble in both organic solvents and water.
- The correct choice of cosmetic products and cleansers is very important to improve skin hydration, to provide moisturizing benefits and to minimize cutaneous damage caused by surfactants.
- Cleansers have the indispensable role to remove dirt, sebum, sweat, microorganisms and exfoliated corneum cells from the skin

# Surface Active Agents



# Surfactant

- “surfactant” applies to a group of molecules having both a hydrophilic part and a hydrophobic (or lipophilic) part.
- Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface and also lower the interfacial tension between oil and water by adsorbing at the liquid–liquid interface

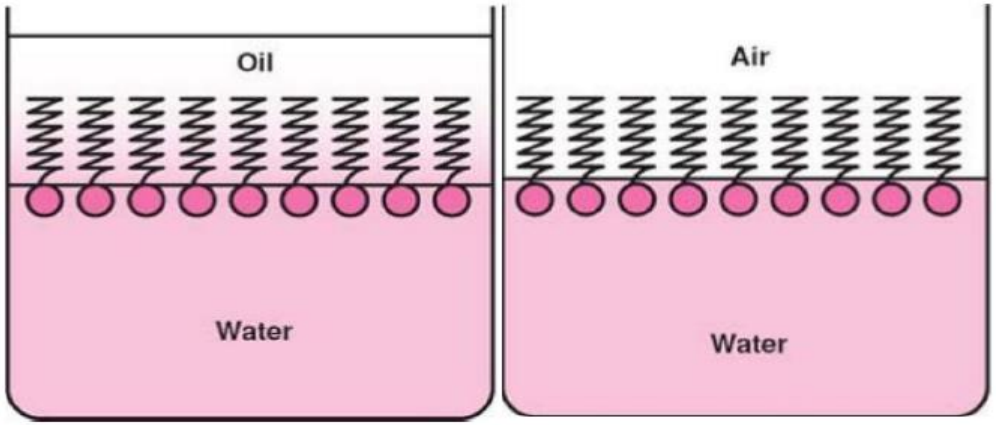



*Figure 1: Adsorption of fatty acid molecule at a water-oil interface (left panel) and a water- air interface (right panel).*

# Surfactant

## Definition

### Surface Active Agent

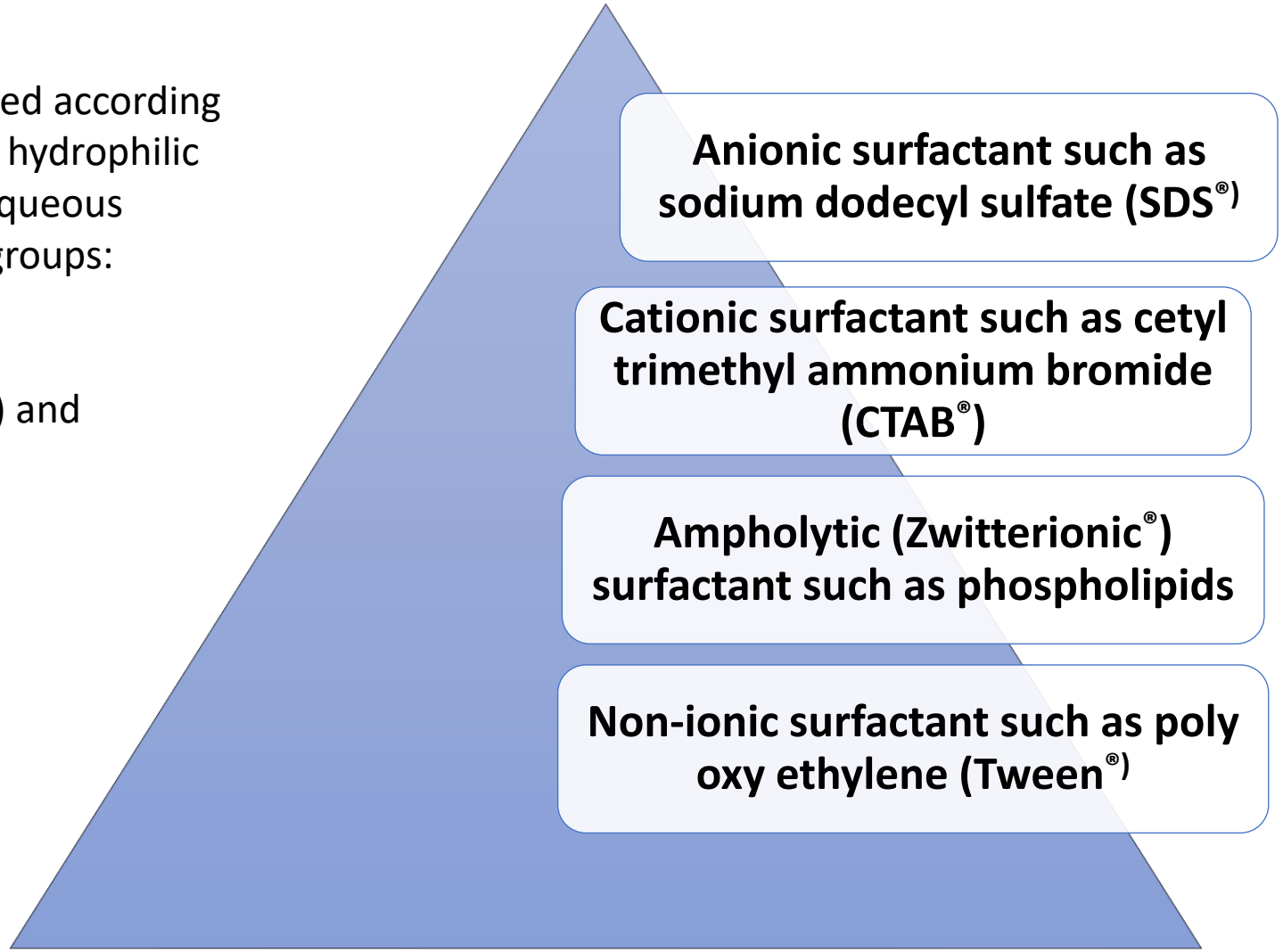
- ✓ Substance which reduces surface/interfacial tension between two phases
- ✓ Compounds having tendency to gather around the interface between two different materials by altering the properties of interface remarkably
- ✓ Serves as good mediator to settle dispute between two phases which are not friends

# *Surfactants are classified*

According to their chemical structure and, more specifically, their polar group:

Surfactants can be categorized according to the charge present in the hydrophilic head (after dissociation in aqueous solution) into four primary groups:

- anionic,
- cationic,
- amphoteric (dual charge) and
- nonionic



# Anionic Surfactants

- Anionic agents possess a **negative charge of their hydrophilic head**.
- The members of this group have the highest cleansing power, good wetting properties, excellent lather characteristics, but moderate disinfectant properties, and
- they are commonly used as primary surfactants in cleansers, because their moderate the final product cost.
- Anionic agents are considered potent irritants to skin
- Ex: alkyl sulphate(sodium lauryl sulphate (SLS)), alkyl ethoxy sulphate((sodium laureth sulphate, SLES) ), acylglutamates, alkyl taurates and alkyl sulfosuccinates
- SLS & SLES is the favourite primary surfactant in body wash/shower gel and shampoo, because of its good cleansing power and its low cost, even if it has some irritant potential

# Cationic surfactants

- positively charged,
- have lower detergent properties than anionic surfactants.
- considerable bactericidal activity against a wide range of microorganisms, they may be used as antimicrobial preservatives rather than as surfactants. equally irritating, but more cytotoxic than anionics
- amine salts and quaternary ammonium salts (cetrimide and benzalkonium chloride).
- Cetrimide solutions (0.1% to 1%) may be used for cleaning wounds and burns on the skin, for disinfection of medical instruments and as hair-conditioning agent in shampoo.
- Benzalkonium chloride (0.5% to 2%) is also used as a preservative for ophthalmic products

# Amphoteric surfactants

- Amphoteric surfactants exhibit the properties of anionics or those of cationics, according to the pH of the solution
- reputedly less aggressive than anionic surfactants & threrfore they are used in combination to enhance mildness
- good cleansing power and lather characteristics, a moderate antimicrobial activity, the lack of toxicity and compatibility with different pHs
- extensively used in liquid cleansers, moisturizing body wash, shower gel, shaving products, shampoo, toothpastes, contact lens detergents
- Commonly used amphoteric surfactants include cocamidopropyl betaine, cocoamphoacetate and cocoamphodiacetate

# Nonionic surfactants

- Nonionic agents have no electric charge in its head
- relatively low potential toxicity and
- they are considered the most gentle surfactants,
- but they are also the most expensive
- used as thickeners for shampoos, as emulsifiers and suspending agents in cosmetics, pharmaceutical products and foods

# Surfactants: Effects

- Cleansing, to remove dirt from skin and hair
- Foaming, to enhance lather in bath foam and shampoo. Some surfactants types have greater foaming power
- Wetting, to increase the contact between the product and the substrate (dirt)
- Emulsifying, to arrange itself at interface between two immiscible liquids. This permits emulsions preparation
- Solubilizing, to introduce insoluble substances in preparations where it needs to preserve the clearness.

# Damaging Effects of Surfactants on Skin

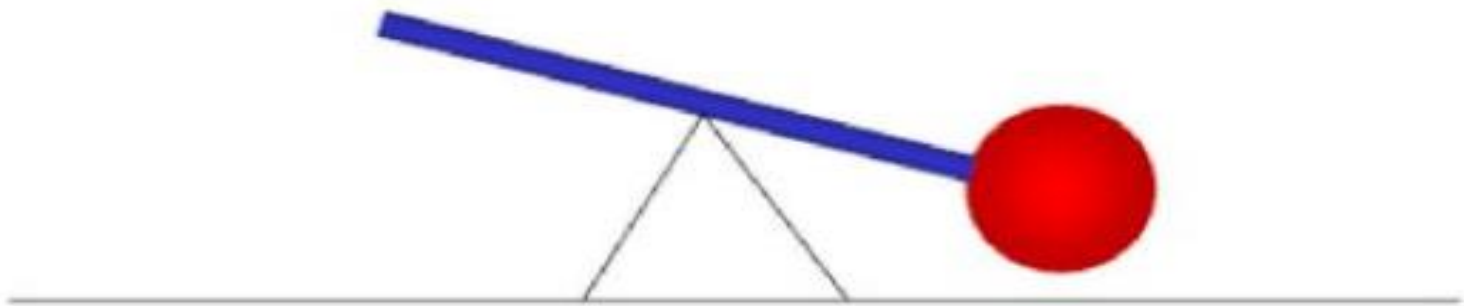
damaging effects include:

- surfactants may also damage protein structures and solubilize lipids.
- protein denaturation,
- **Delipidation**: the ability of surfactants to solubilize lipid membranes
- inflammatory processes with keratinocyte-derived cytokine release
- Swelling of cell membranes and collagen fibres, resulting from damaging effects for skin proteins
- **Alkalization** is an intrinsic feature of these common soaps
- Cytotoxicity &Irritation

| Surfactant type | Example | Use |
| --- | --- | --- |
| **Anionic** | Alkyl sulfates, soaps, Calsoft®, Texapon® | 50 % of overall industrial production, laundry detergent, dishwashing liquids, shampoos |
| **Cationic** | Quaternary ammonium salts | Used together with nonionic surfactants but not with anionic, softeners in textiles, anti-static additives |
| **Nonionic** | Ethoxylated aliphatic alcohol, polyoxyethylene surfactants, Triton™ X-100, Span®, Tergitol™ | 45 % of overall industrial production, a wetting agent in coatings, food ingredient |
| **Zwitterionic** | Betaines, amphoacetates | Expensive, special use e.g. cosmetics |

# HLB –Hydrophilic Lipophilic Balance

## HLB is a means of expressing the hydrophilic property of surfactants in figures

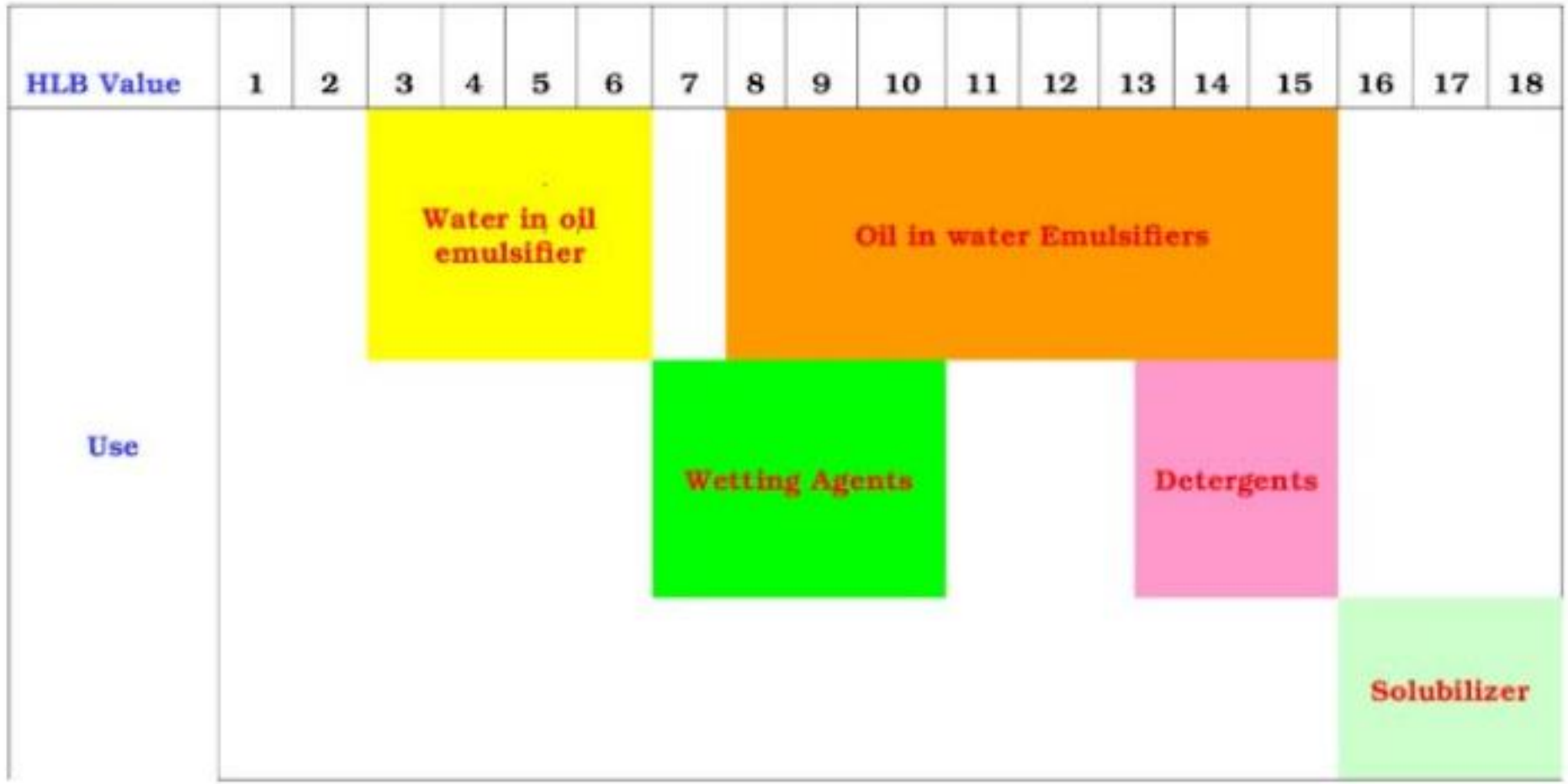


**Low HLB values**
The lipophilic (hydrophobic) part is dominating

**High HLB values**
The hydrophilic part is dominating

# HLB Value

## Significance

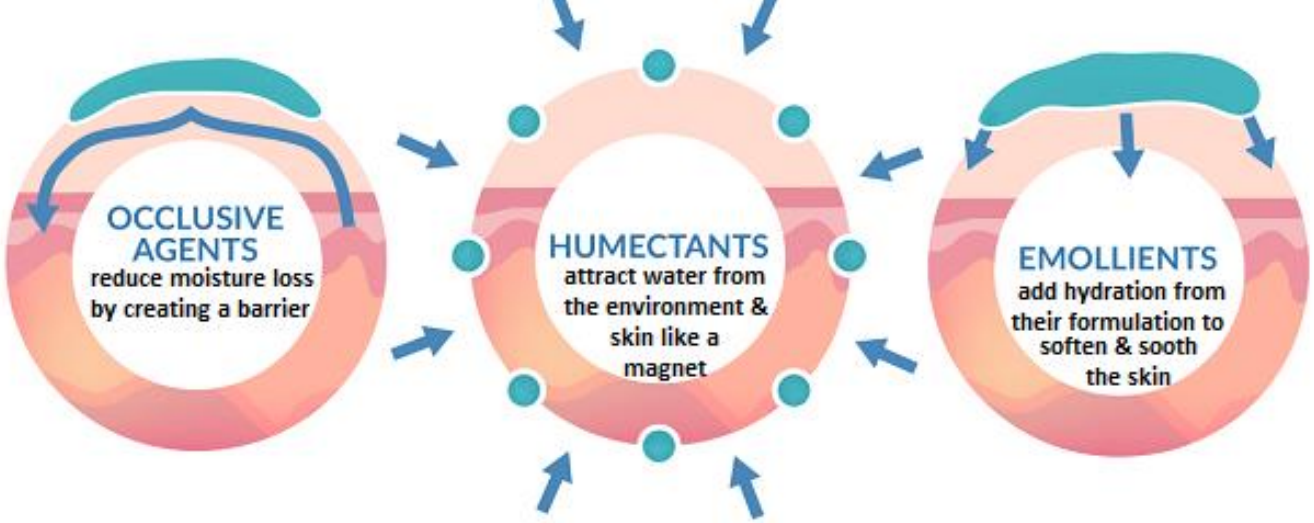


# Emollients:
# Building blocks of skin care products

# Definition

- Emollients are normally defined as ingredients that impart a smooth, soft, or lubricious feeling to skin. The term emolliency usually refers to the spreading and lubricity on skin or hair as a function of time.
- Emollients are among the most common ingredients used in personal care formulations.
- The word emollient is derived from the Latin word *mollis* or *molle,* which means soft, pliable, and supple.

# Emollients




- is a humectant, a lubricant & an occluder.
- Occlusion puts a layer of oil on the skin's surface, slowing down the water loss.
- Humectant enhances the surface of the skin's capacity to hold water.
- Lubricant reduces friction when anything rubs against the skin.
- They reduces water loss from the outer layer of skin (epidermis) by covering it with a protective film.
- Emollients are the topical treatment that are applied directly to the skin. They are mainly lipids and oils, which hydrate and improve the skin softness, flexibility, and smoothness.

# Emollients

- are typically lipids (fats and oils) that can improve the appearance of the skin by filling in defects between skin cells, and make the skin more soft and flexible.
- Examples include lanolin, paraffin, ceramides, and silicones.
- Many emollients are also humectants, and both can fill irregularities in skin texture to rapidly improve the texture and appearance of skin.
- Some emollients such as mineral oil or castor oil can also function as barriers/occlusive.

# Benefits of emollients

- Modify skin feel: skin feel correlates closely with molecular weight (MW) and viscosity
- Provide shine to skin, hair, and lips: the refractive index of an emollient correlates well with skin shine
- Condition hair: mainly use high MW Silicone fluids (>100K cSt.)
- Act as the main formulation carrier in anhydrous formulations
- Act as an active solvent: generally high polarity emollients are preferred
- Thicken anhydrous, oil in water, and water in oil formulations
- Moisturize, skin, and improve skin elasticity
- Reduce skin moisture loss (transepidermal water loss, or TEWL)
- Modulate active skin delivery
- Can reduce the appearance of wrinkles
- Can increase cell turnover

# Mechanism of emollients

- Occlusion: These work by forming a thin film on the surface of the skin to prevents loss of water.
- Restoration of deficient materials: They are more complex and try to restore natural moisturizing factors on the skin such as amino-lipids.
- Antimitotic: Slow the process of mitosis on the epidermis by mineral oil which could be helpful for people who have psoriasis disease.
- Inhibit proinflamamatory prostanoids production: blocking cyclooxygenase activity which causes soothing and lower skin inflammation.

# Classification of emollients

1. On the basis of natural origin
2. On the basis of properties of excipients
3. On the basis of function

# 1. On the basis of natural origin

| Plant Derived emollients | Animal Derived emollients | Bioactive Emollients |
|---|---|---|
| • Castor oil<br>• Squalane<br>• Jojoba oil<br>• Cocoa butter<br>• Shea butter<br>• Argan oil | • Lanolin<br>• Beeswax | • Soline<br>• Avocadin HU25<br>• N G Shea Unsaponifiable |

Argan oil


Shea butter


Cocoa butter

Squalane

Jojoba oil

# 2. On the basis of properties of excipients

| Dry emollients | Fatty emollients | Astringent emollients | Protective emollients |
| --- | --- | --- | --- |
| • Decyl oleate<br>• Isopropyl palmitate<br>• Isostearyl alcohol | • Castor oil<br>• Glyceryl stearate<br>• Jojoba oil<br>• Octyl stearate<br>• Propylene glycol | • Cyclomethicone<br>• Dimethicon<br>• Isopropyl myristate<br>• Octyl octanoate | • Diisopropyl dilinoleate<br>• Isopropyl Isostearate |

# 3. On the basis of function

## 1. Non Medicated Topical Emollients

Non medicated emollients contain occlusive agents (Fat soluble emollients) humectants (water soluble emollient).

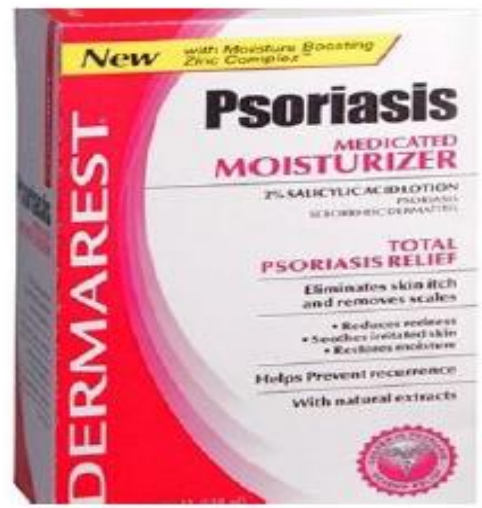
Emollients offer an occlusive barrier and they smooth flaky skin cells, to make the skin look smoother. Some spread more easily than others.

Esters and oils can be used.

# 2. Medicated emollients

Some emollients contain specially medicated formulas that can be used to treat skin condition such as eczema , psoriasis.

Medicated emollients for psoriasis and eczema may contain **corticosteroids, salicylic acid, vitamin D analogs, coal tar, tazarotene, anthralin, tacrolimus, pimecrolimus.**

# Ceramides & Squalene

CERAMIDES: In (SC) ceramides are major lipid constituents and along with neutral lipids, they form board laminated intercellular sheets, which act as barriers to our environment.

Natural ceramides or synthetics are too expensive,so **pseudo-ceramides** are used.

SQUALENE: It is component of Human sebum.

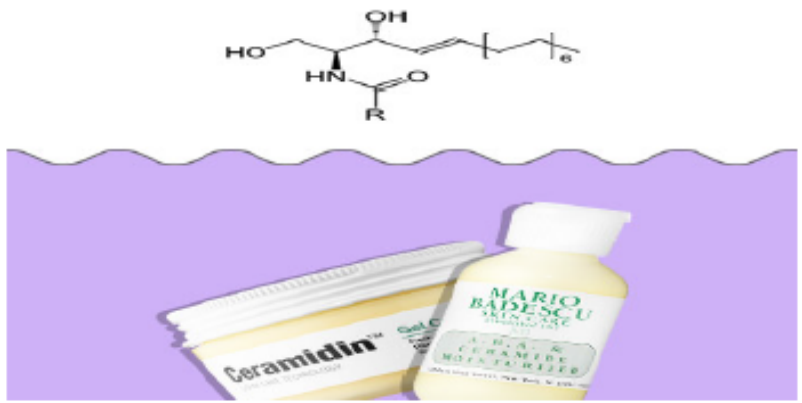
It act as quencher of singlet oxygen protecting human skin surface from lipid peroxidation due to exposure to UV and other sources of ionizing radiation.

Squalane is saturated form of squalene in which the double bonds have been eliminated by hydrogenation.Squalane is less susceptible to oxidation than squalene,so mostly used as moisturizer.

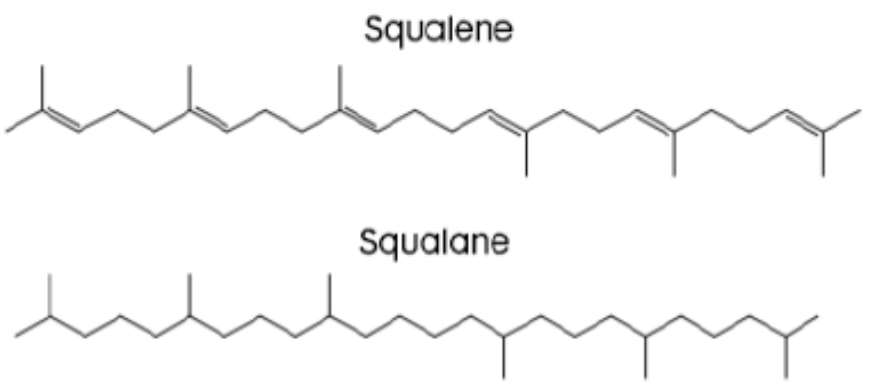
Properties: It is technically oil, it doesnot have oily feel ,is odorless noncomedonal ,antibacterial and is safe for sensitive skin.

Use: For treating skin disease , such as seborrheic dermatitis, acne, psoriasis, atopic dermatitis.

CERAMIDES




Chemical Structures of Squalene and Squalane



- Ceramides are **a family of waxy lipid molecules**. A ceramide is composed of sphingosine and a fatty acid. Ceramides are found in high concentrations within the cell membrane of eukaryotic cells

# Applications

## 1. Preservation of normal skin:

- Prevent the skin from becoming too dry or oily
- Improve skin tone and texture and mask imperfections.

Eg: cetyl alcohol
Silicone- derived ingredients i.e cyclomethicone

## 2. Dry skin:

- More effective to prevents water evaporation
- Heavier oils based moisturizer that contain ingredients such as antioxidants
- For very dry skin, craked skin

Eg: petroleum based used cetaphil, putraderm

3. **Sensitive Skin:**

- Which is susceptible to skin irritations,redness, itching rashe.
- Minimise the potential allergens such as fragrances or dyes

Eg: Aloe,Chamomile

4. **Eczema**: Characterized by dermatitis,inflamation of skin, redness itching, blister like skin thickened.

Eg: Treatment of emollients and steroids

Dexamethasone , Vit D, ceramides recently used major lipid constituents.

Commonly used emollients for eczema :

1. Eucerin Daily replenishing moisturizing lotion
1. Aquaphor Healing Ointment
2. Moisturel Therapeutic lotion.

# 4.ECZEMA

Characterized by dermatitis,inflamation of skin, redness itching, blister like skin thickened.

Eg: Treatment of emollients and steroids

Dexamethasone , Vit D, ceramides recently used major lipid constituents.

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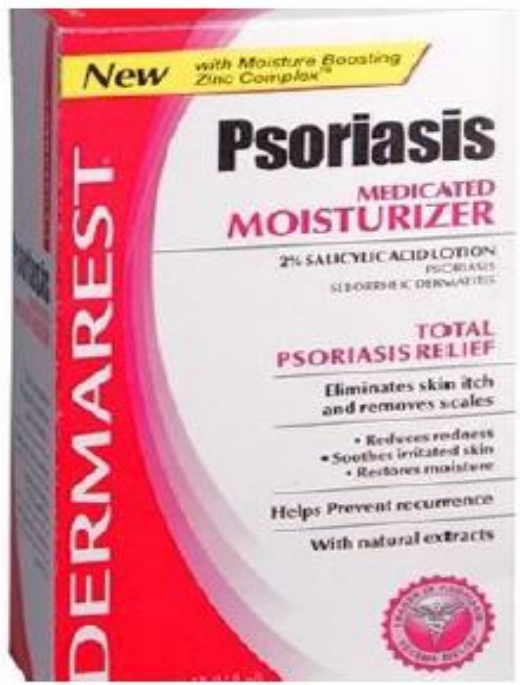
# 5. PSORIASIS

A condition in which skin cells build up and form scales and itchy dry patches.

Emollients in psoriasis:

1. Dermarest psoriasis Medicated
2. Careve Moisturing cream
3. Eucerin skin caliming itch relief

# RHEOLOGICAL ADDITIVES

- What is rheology/viscosity
- How to measure viscosity
- What are different types of flow
- What are different rheological additives

# Rheology & Viscosity


- Rheology: The study of the change in form and the flow of matter, embracing elasticity, viscosity, and plasticity.
- Viscosity– It is resistance to flow and measured by the ratio of shear stress to shear rate .

# Cosmetics and Rheology

- **Rheology is the science of flow.**
- **Every time a lotion is poured, a cream squeezed from a tube or a lipstick applied, rheology is involved.**
- **Even when products are at rest, it plays an important part in controlling stability and suspension.**
- **Understanding a formulation's rheological needs enables you to create the best possible products.**
- **The rheology of a system is described in terms of its viscosity.**

# Viscosity

- **Viscosity is the resistance to flow and**
- **Defined as: Shear stress is the force per unit area applied and shear rate is the resulting velocity gradient.**

$$\text{Viscosity} = \frac{\text{Shear stress}}{\text{Shear rate}}$$

- **Cosmetics experience shear rates varying from 0.001 s-1, from gravitational forces;to over 20,000 s-1, when a cream is spread oran aerosol antiperspirant sprayed .**

# Types of Flow

**Newtonian flow**

**Non Newtonian flow**

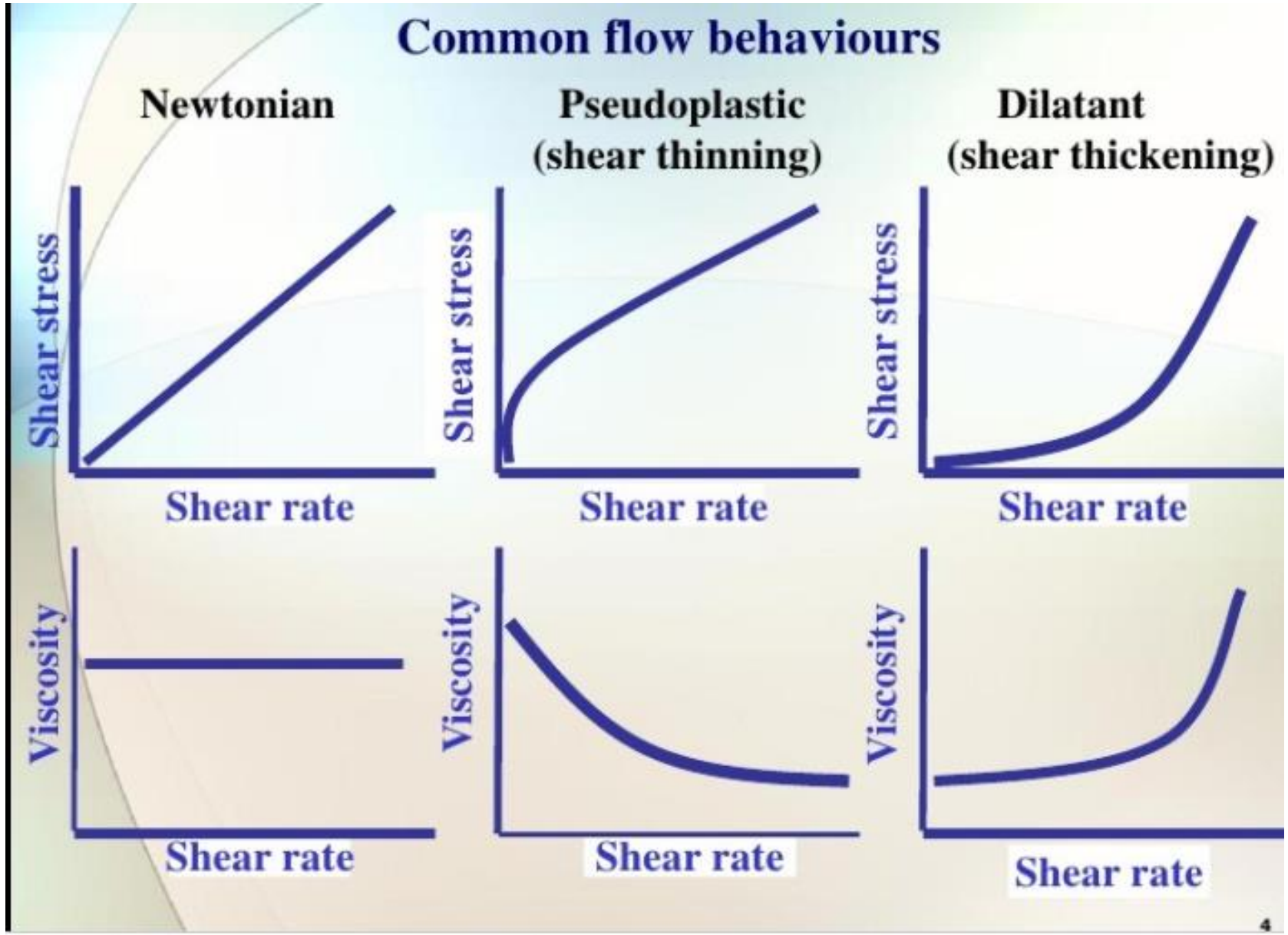
# Types of flow/viscosity

## Newtonian flow

In Newtonian flow, the viscosity remains constant, no matter the amount of shear applied for a constant temperature.

These fluids have a linear relationship between viscosity and shear stress.

**A material which maintains a constant viscosity, regardless of shear rate, has Newtonian flow.**

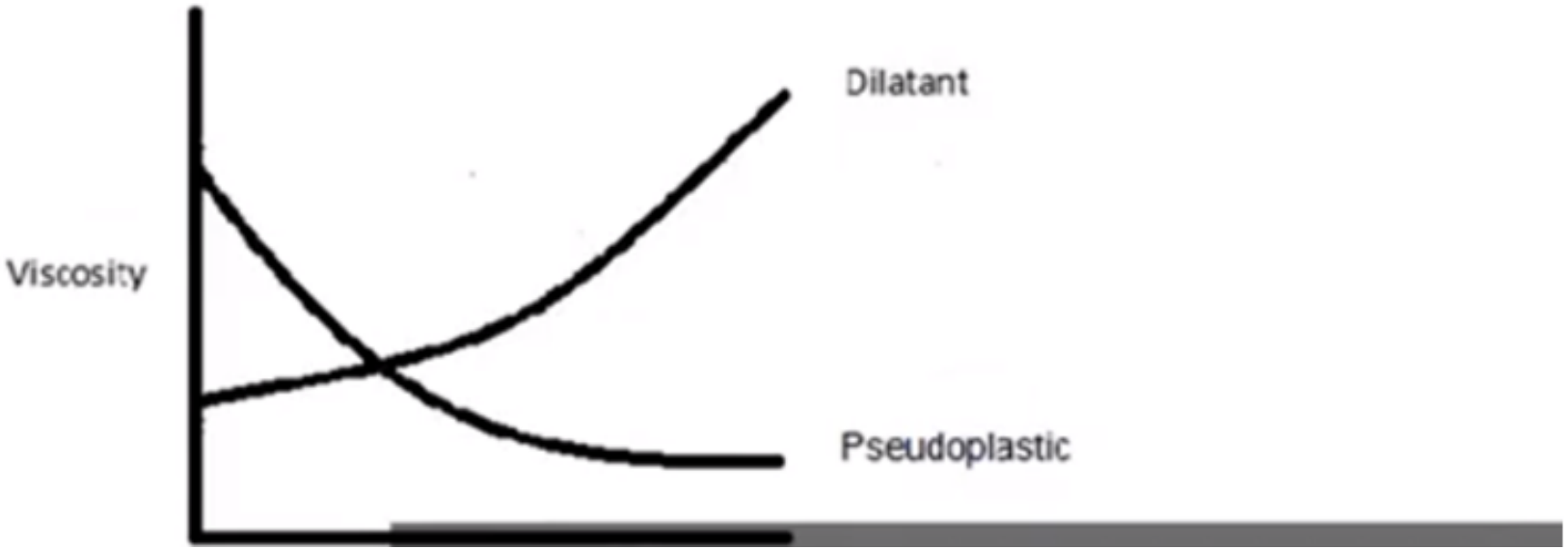

Common flow behaviours
Newtonian
Pseudoplastic
(shear thinning)
Dilatant
(shear thickening)
Shear stress
Shear rate
Shear stress
Shear rate
Shear stress
Shear rate
Viscosity
Shear rate
Viscosity
Shear rate
Viscosity
Shear rate
4

## Non-Newtonian flow

When shear is applied to non-Newtonian fluids, the viscosity of the fluid changes.

**Dilatant**- Viscosity of the fluid increases when shear is applied. For example quicksand and cornflour.

**Psuedoplastic-** Viscosity of fluid decreases with increasing shear. For example ketchup.



- **Rheopectic**- In this type of flow viscosity is time dependent. Ex. Cream and gypsum paste.

- **Thixotropic**- Fluids with thixotropic properties decrease in viscosity when shear is applied. Ex. Paint and glue.

# Cosmetics and Rheology

- **The way the viscosity changes at varying shear rates greatly influences the over all product stability and performance.**
- **Dilatant flow is a form where viscosity increases with shear.**
- **Pseudoplastic flow also known as shear thinning behaviour.**
- **Flow may require a specific stress to be initiated. This particular stress value is known as the yield point. A system having both shear thinning flow and a yield point can be described as having plastic flow.**
- **The rate of recovery of a system when stress is removed is also very important.**
- **When a shear thinning system shows delayed viscosity recovery, it is described as thixotropic flow .**

**Fig. 3**

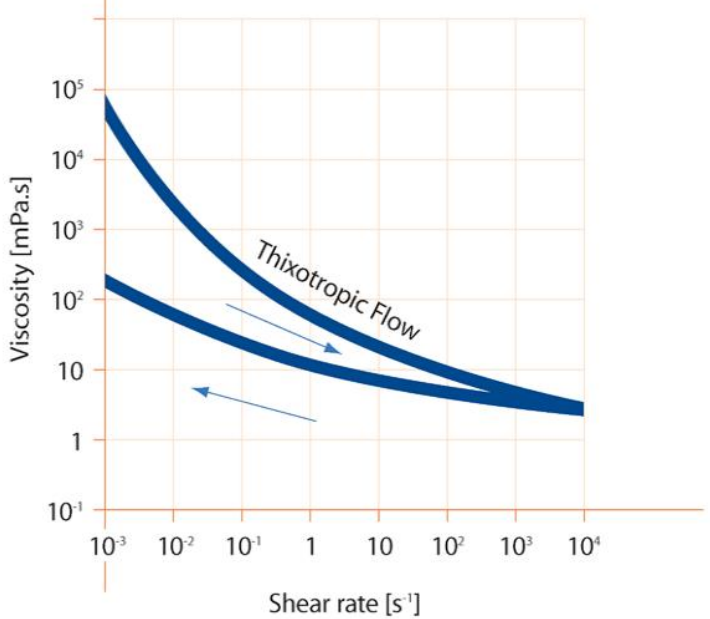
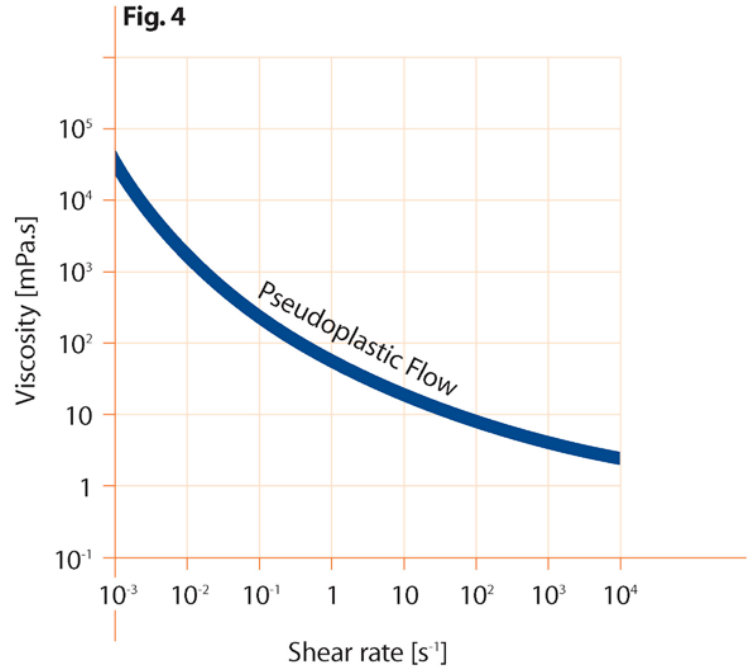

Viscosity [mPa.s]
10⁵
10⁴
10³
10²
10
1
10⁻¹
Thixotropic Flow
10⁻³ 10⁻² 10⁻¹ 1 10 10² 10³ 10⁴
Shear rate [s⁻¹]

**Fig. 4**


Viscosity [mPa.s]
10⁵
10⁴
10³
10²
10
1
10⁻¹
Pseudoplastic Flow
10⁻³ 10⁻² 10⁻¹ 1 10 10² 10³ 10⁴
Shear rate [s⁻¹]

# Measurement of viscosity

- We generally measures two types of viscosity
  - Absolute/ Dynamic Viscosity
  - Kinematic Viscosity
- Proportionality constant between shear stress and velocity gradient is often called as “Dynamic Viscosity / Absolute Viscosity”.

# Dynamic Viscosity / Absolute Viscosity

- Reciprocal of Dynamic Viscosity is “Fluidity”.
- Ratio of Shear stress to the velocity gradient of the fluid is known as Absolute Viscosity.

# Measurement of viscosity

- Instruments which measures the viscosity are called as Viscometers.
    1. Capillary flow viscometer
    2. Circular flow viscometer
    3. Cone & plate flow viscometer
    4. Parallel plate flow viscometer

Modified Natural additives

Plant

| | |
|---|---|
| Wood pulp and cotton | • Cellulose derivatives |
| Seed extracts | • Guar derivatives |

Now, modified natural additives,

# Synthetic additives

**Petroleum based**

- Acrylic acid polymer
- Polyacrylamides

**Inorganic additives**

**Clays**

- Smectite hydrophilic
- Organoclays.

**Amorphous silicon dioxide**

- Hydrated silica,
- Fumed silica