What is Soap ?

Innøleague Training Series

Solving Problems
Creating Value

Questions

- What is a typical Soap's composition ?
- How does it function ?
- How is Soap made ?
- What parameters are important for its marketers?

Appreciation of a Formulator's work

Implications on perfumes

What is Soap Bar's Chemical Structure ?

- Formulation

	% Range	Typical
• Soap		
– TFM : Total Fatty Matter	82-50	78
– Sodium Hydroxide	7-4	6
• Moisture Content	10-14	12
• Superfat	1-2	0.5
• Electrolytes (NaCl, Na2CO3)	0.5-1.0	0.7
• Fillers	0-25	1.5
• Active Surfactants	0-4	0
• Speciality Ingredients e.g.		
» Optical Brighteners	max 0.03	0.03
» Perfumes	~1.5	1.3
» Preservative : Chelating agents	max 0.3	0.3

OLD SYSTEM OF SOAP MANUFACTURING

Oil + Caustic → Soap + Glycerine

OIL

→ Lauric Oils / Non Lauric Oils

Lauric Oils

- CNO
- CNO Acid Oil
- PKFA
- Myristic acid

Non Lauric Oils

- RBO
- HRBO
- Karanjia
- Neem
- Castor Oil
- Palm
- Cotton seed
- Tallow

NEW SYSTEM OF SOAP MANUFACTURING

Oil + Water → Crude Fatty Acid + Glycerine

Crude Fatty Acids are then Distilled to remove impurities

Distilled Fatty Acid + Caustic → Soap + Water

Fatty Acids

Lauric Oils- Fatty Acids

CNO
CNO Acid Oil
PKFA
Myristic acid

Non Lauric Oils- Fatty Acid

Rice Bran Oil
Hydrogenated RBO
Karanjia
Neem
Castor Oil
Palm & Palm Fractions
Cotton seed
Tallow

CHEMICAL EQNS

Oil **+** **Caustic** → **Soap** **+** **Glycerine**

Oil		Caustic		Soap		Glycerine
CH-OR | CH2-OR | CH-OR		3 NaOH	→	RCOONa		CH-OR | CH2OR | CH-OR

Fatty Acid **+** **Caustic** → **Soap** **+** **Water**

Fatty Acid		Caustic		Soap		Water
RCOOH		NaOH	→	RCOONa		H2O

Properties and Composition of Vegetable and Special Oils

		Rapeseed Oil low erucic	Groundnut Oil	Cottonseed Oil	Corn Oil	Tung Oil	Palm Oil	Olive Oil	Rapeseed Oil high erucic	Castor Oil	Tall oil southern US crude	Tall oil Fatty acids crude	Tall oil Fatty acids <2% rosin
Iodine value		105 - 120	84 - 100	99 - 113	103 - 128	160 - 175	44 - 54	80 - 88	91 - 108	81 - 91			
Saponification value		185 - 198	188 - 195	189 - 198	187 - 193	189 - 195	195 - 205	188 - 196	170 - 185	176 - 187			
Titer °C		5 - 15	26 - 32	30 - 37	14 - 20	36 - 37	30 - 38	17 - 26	15 - 23	3 - 5			
Unsaponifiables %											6 - 10	2.5	1.5
Fatty acid											42-55		
Rosin acid											33-47	7	1
Butyric acid	C 4												
Caproic acid	C 6												
Caprylic acid	C 8												
Capric acid	C 10												
Lauric acid	C 12												
Myristic acid	C 14	0 - 2	0 - 1	0 - 2	traces		0 - 2	0 - 1	traces				
Pentadecanoic acid	C 15												
Palmitic acid	C 16	1 - 5	6 - 16	17 - 29	7 - 12	3 - 4	32 - 45	7 - 15	0 - 5	1 - 2		1.6	
Heptadecanoic acid	C 17											0.7	
Oleic acid	C 18:1	50 - 66	36 - 72	13 - 44	35 - 50	4 - 9	38 - 52	65 - 85	9 - 25	4 - 9		42.3	
Linoleic acid	C 18:2	18 - 30	13 - 45	33 - 58	35 - 50	8 - 10	5 - 11	4 - 15	11 - 25	2 - 7		34.8	
Isomers	C 18:2											12.7	
Linoleic acid	C 18:3	6 - 14	0 - 1	0 - 2	0 - 1			0 - 1	5 - 11	0 - 1			
Eleostearic acid	C 18:3					77 - 86							
Licanic acid	C 18:3												
Stearidonic acid	C 18:4												
Gadoleic acid	C 20:1	0 - 5	1 - 2						5 - 15	traces			
Eicosadienoic acid	C 20:2											4.7	
Eicosatetraenoic acid	C 20:4												
Eicosapentaenoic acid	C 20:5												
Erucic acid	C 22:1	0 - 5							30 - 60				
Docosapentaenoic acid	C 22:5												
Docosahexaenoic acid	C 22:6												

All Oils = Glycerol + Mixtures of Fatty Acids (organic carboxylic acids)

Organic Carboxlic acids ≠ Inorganic acids like HCl etc but like acetic

IMPORTANT CHARACTERISTICS For SOAP MAKING

- Saturated Fatty Acids

Name	Chain Length	MP °C	Usefullness
Butyric	C4	- 8.0	Not required
Caproic	C6	- 2.0	Not required
Caprilic	C18	16.5	Lather/Process aid
Capric	C10	31.3	Lather/Process aid
Lauric	C12	43.6	Lather/Process aid
Myristic	C14	53.8	Lather
Palmitic	C16	62.8	Body structure
Stearic	C18	69.0	Body structure
Arachidic	C20	75.3	Not required
Behenic	C22	79.8	Not required
Lignoceric	C24	84.1	Not required

UNSATURATED FATTY ACIDS : EFFECTS

Double Bond

One can see the affect of introduction of a unsaturation in fatty acids

Name	Chain Length	MP °C	No. of double bonds	Position
Stearic	C18	69.9	0	0
Oleic	C18	16.0	1	9 – 10
Linoleic	C18	-5.0	2	0 – 10, 12 - 13
Linolenic	C18	-11.0	3	9-10, 12-13, 15-16

- Linoleic / Linolenic are useless for dirt removal / lather
- Added disadvantage of perfume stability (PUFA bad for Soap stability)
- Oleic is most important, attracts equal amount of Laurates/Myristates to form soap which can go in liquid phase to give excellent lather attributes.

HISTORY Vs IDEAL SOAP FAT CHARGE

- Universally by accident, good soap was discovered.
- Like any other natural resource, related science unfolded after 1900 to explain properties.
- Ideal soap - 60/ 78 TFM made from 20 CNO / 80 Tallow
  Gives all soap user attributes.

- **FA composition**

FA composition	%	Unsaturation
C8 - C10	2.6	0
C12 Lauric	9.6	0
C14 Myristic	3.8	0
C16 Palmitic	22	0
C18 Stearic	25	0
Oleic	34	1
Linoliec	3	2
Linolenic	0	3

GOOD SOAP vs SOAP STRUCTURE

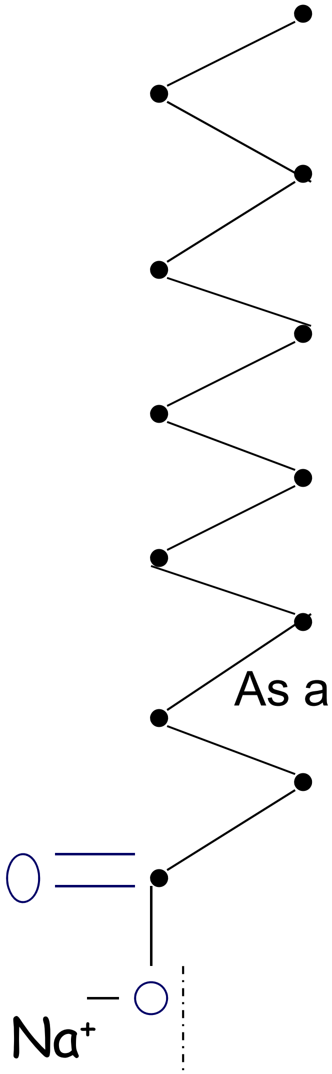
- Good Lathering
- Good feel
- Economy in use
- Long shelf life
- Excellent presentation

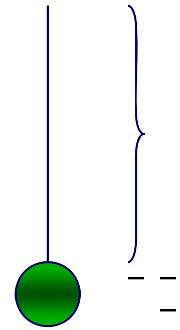
Cleaning - dirt removal.
Good colour
Good perfume
Easy to handle shape

Last two are aesthetics.

- Very difficult to find one single molecule satisfying all these properties and hence - fat charge selection.
- Point proved beyond doubt by 78 TFM - Laurate/Myristate
  - Palmitate / stearate
  - Nil Lather / Nil ROW

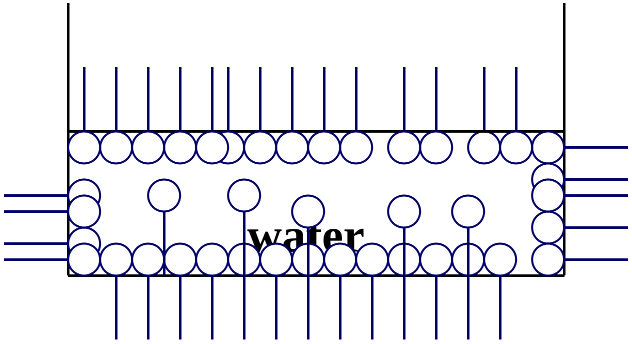
VISUALISE SOAP MOLECULE

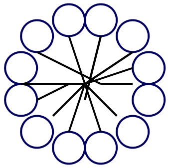




As anion is responsible soap is called anionic detergent.

Micellisation

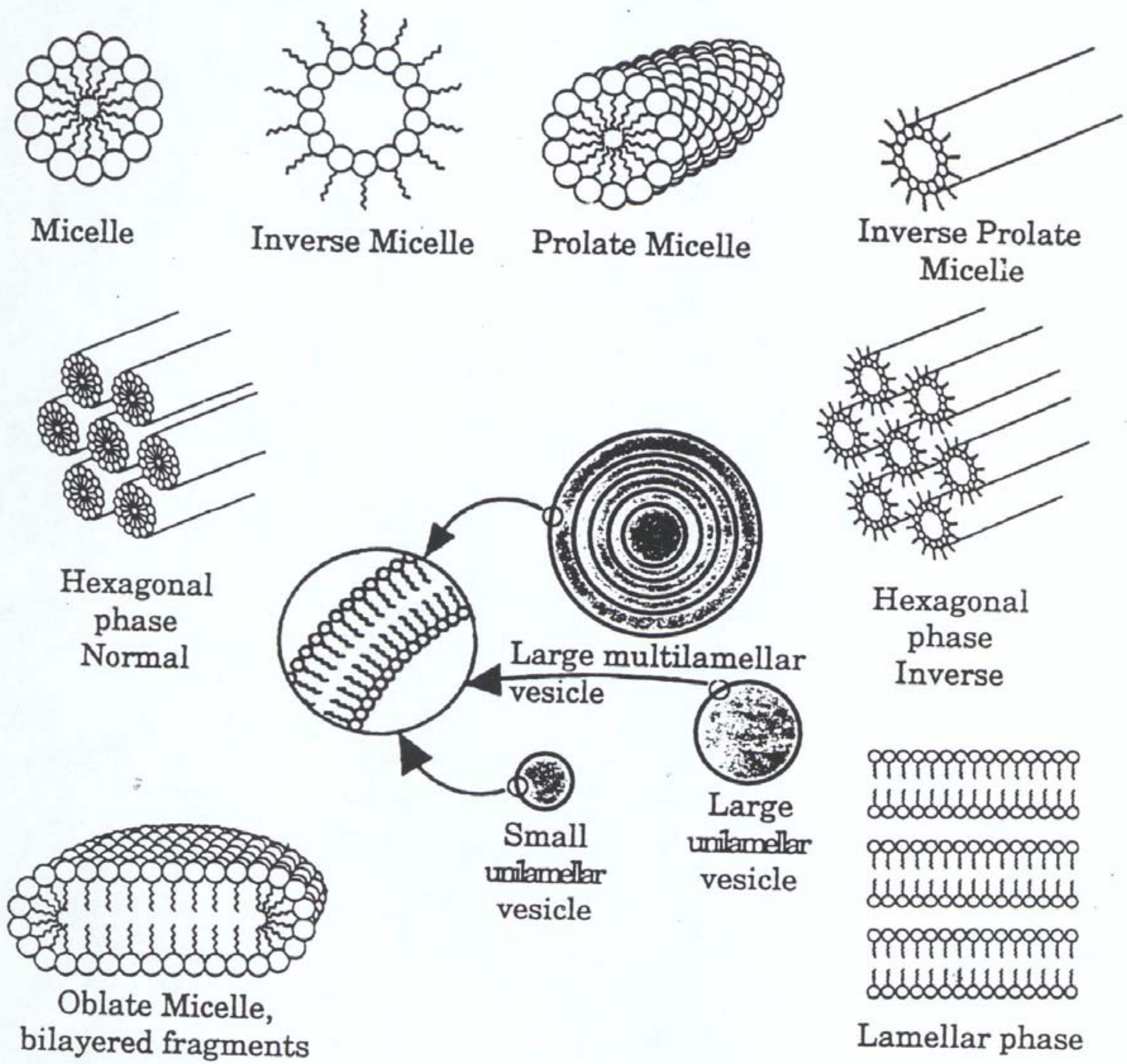




Surface Tension drops with increasing Soap conc, become flat at CMC

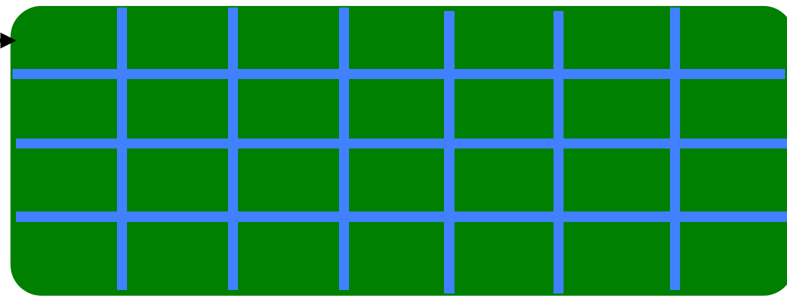
Low Surfacre Tension = More penetration of water into cloth fibres or surface of skin to clean inorganics

Micelles solubilize organic dirt inside and remove


Micelle
Inverse Micelle
Prolate Micelle
Inverse Prolate Micelle
Hexagonal phase Normal
Hexagonal phase Inverse
Large multilamellar vesicle
Small unilamellar vesicle
Large unilamellar vesicle
Oblate Micelle, bilayered fragments
Lamellar phase

Formulation Principles

BRICK
Palmitates,
Stearates,
Myristates(50)



MORTAR
Oleates, Laurates,
Myristates(50)

Conventional Soap (78 tfm) :

78 tfm , 38-40 IV - 13 mc max (processability issues)
soluble phase :
* moisture 13
* eutectic mixture of fats 16

total = 29

Structured Soap :

seeks to replace insoluble brick fat by structurants

Formulation Principle

- Formulation

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Which Parameters are important?

- Formulation
  - TFM
  - IV
  - CNO
  - Moisture Content
  - Superfat
  - Electrolytes
  - Fillers
  - Active Surfactants
  - Speciality Ingredients e.g. Polymers
- Environmental
  - Ageing
  - Temperature Profile
  - Humidity

Parameter mapping

Thumb Rules

↑	% Wear	MVA/MBI	Lather	PV
TFM	↓	-	↑	↓
CNO	-	↑	↑	-
Superfat	-	↑	↑	↓
IV	↑	↑	↑	↑
MIV	↑	↑	-	↑
NaCl content	↓	-	-	↓

Gross Negatives

- Cracking
- Efflorescence
- Perfume Interaction
  - due to chemical reactions between different ingredients viz. aldehydic, ketones and esters, trace metals from packaging materials and aromatic organic compounds in printing inks
- Grit
  - Soap grit :due to improper process conditions, detectable only in cold water
  - Chemical grit : oversize particulate

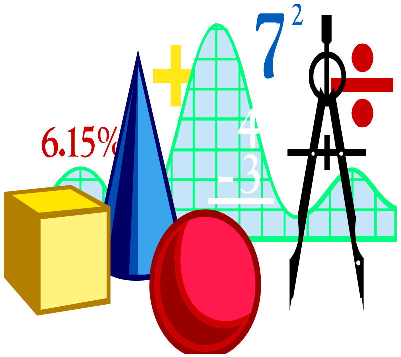
Implications on Perfume

Product Formulation

- TFM
- Structurant/ inorganic compounds e.g. Soda Ash, Salt, Phosphates etc
- Organic compounds e.g. Glycerin, surfactants, starch derivatives, color
- Water
- Perfume

Outer Packaging

- Stiffener
- Packaging substrate
- Printing inks



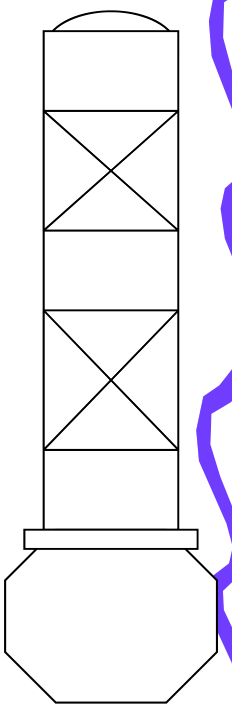
Understanding role of TFM

- Major portion of all soaps: Majority of perfume goes in masking off-odors generated by this component

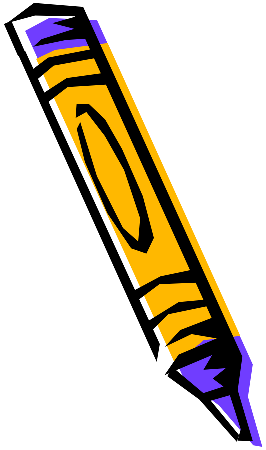
- Fatty Acids <c12 have characteristic sharp odor (unpleasant)
    - Removed during distillation using new structured packing technology

- Improper Distillation op parameters => unpleasant odor i.e.burnt, acrid if residence times high => FFR distillation column

- Pretreatment of Oils must to remove Proteinaceous materials



Odors in Oils : Understanding them



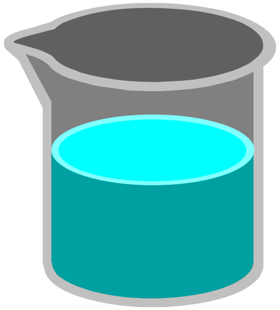
- Influenced by the type and quality (Freshness) of oil

- Concept of Natural odors vs. Degradation odors

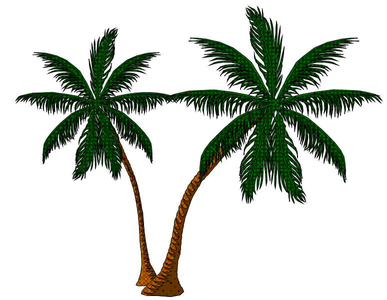
- Natural Odors are characteristic of a particular Oil

- For removal of Natural odors identification of characteristic odoriferous bodies for individual oils a must

- Set distillation parameters to ensure separation of these odor bodies from bulk cut by
    - Providing adequate number of fractionating stages
    - Condenser temperatures
    - Pretreatment of oil



Natural Odors by Oil type



Characteristic odors of Lauric fractions:

Typical coconut like : Delta Octalactone
Heavy, nutty, oily : Delta Dodecalactone
Oily, old nutty : 2 Tridecanone

Characteristic odors of Palm fractions

Metallic mushroom : 1 Octene-3-one
Germanium metallic : Cis 1,5 Octadiene-3-one

Characteristic Odors of Rice Bran Oil

Husky, Branny, Spicy : Isoeugenol, Eugenol, Guiacol derivatives

Degradation of TFM

Saturated Fatty Acids are not prone to oxidative degradation however sensitive to Pyrolysis

Primary cause of degradation is the autoxidation of unsaturated fatty acids (PUFA)

Rate of autoxidation increases with degree of unsaturation
C18:3 is 30 times faster degrading than
C18:1 and C18:2 is 10 times faster than C18:1

All the above decomposition resultant products are short chain unsaturated fatty acids, Hydrocarbons, alcohols or carbonyl group compounds viz. **aldehydes & ketones**

Degradation Mechanisms

Free radical Autoxidation of unsaturated fatty acids
(Chain Reaction)

Initiation :

-CH-C=C- => -C*-C=C- + H* (Heat, light, transition metals)

Propagation

R* + O_2 => ROO*

ROO* + RH => ROOH + R* (ROOH Hydroperoxide)

Termination

R*+R* => R-R

R* + ROO* => ROOR

ROO* + ROO* => ROOR + O2

Degradation Mechanisms

Free radical Autoxidation of unsaturated fatty acids

-CH-C=C- => -C*-C=C- + H* (Heat, light, transition metals)

The resultant allyl radical is stabilized due to delocalization of π electrons over 3 Carbon atoms for C18:1 and 5 Carbon atoms for C18:2 (Resonance effect)

-C*-C=C <=> -C=C-C* = -C-C-C

-C=C-C*-C=C- <=> -C*-C=C-C=C <=> -C=C-C=C-C*-

= -C-C-C-C-C-

Above explains the different rate of reactions for the three species

Degradation Mechanisms

Free radical Autoxidation of unsaturated fatty acids

-The different hydroperoxides produced are

•C18:1 a mixture of 8-,9-,10-,11 allylic hydroperoxides

C18:2 a mixture of conjugated 9- and 13- hydroperoxides

C18:3 a mixture of diene-triene 9-,12-,13- and 16- hydroperoxides

Degradation Mechanisms

Free radical Autoxidation of unsaturated fatty acids

Hydroperoxides are unstable and decompose

1. R-CH(OOH)-R => R-CH(O*)-R +OH*
   R-CH(O*)-R => R-CHO +R*   and so on

2. R-CH(OOH)-R => R-CH(O*)-R +OH*
   R-CH(O*)-R => R-CO-R +H*   and so on

Final Degradation products

Oleate : 8-hydroperoxide => 2 Undecanal and decanal
9-hydroperoxide => 2 Decenal & Nonanal

Linoleate: 9-Hydroperoxide => 2,4 decadienal & 3-Nonenal
13-Hydroperoxide=> Hexenal

Degradation Mechanisms

Singlet Oxygen Mechanism

- Singlet oxygen reacts readily with PUFA
- generated by exposure to light in the presence of photosensitizes like Chlorophyll and transition metals etc.
- Oxygen added directly across the double bond by “ene reaction”
- Produces allylic hydroperoxides

Effect of Metals

- Metals initiate Fatty Acid- Oxygen reactions and form colored complexes
- The anion formed can either lose an electron to give singlet oxygen or react with a proton to form hydroperoxy radicals
- $M^{+} + O_2 \Rightarrow M^{2+} + O_2^{*}$

$$O_2^{*} \xrightarrow{e^-} 2\,O^{*}$$

$$O_2^{*} \xrightarrow{H^{*}} HOO^{*}$$

Antioxidants

Five Categories

- Primary antioxidants : Terminate free radical reactions e.g. TBHQ, BHT etc.

- Synergists : Boost activity of primary antioxidant

- Oxygen Scavengers e.g. Ascrobic Acid

- Biological Antioxidants (natural) e.g. Tocopherols Vitamins

- Chelating Agents : Complexes the metal ions and render them inactive as catalysts e.g. EDTA, EHDP, Citric Acid

Effect of Temperature

- Higher Temperatures = More rapid degradation
  - Rate of Reaction is that much faster

- Longer Exposure to High Temperature = Faster Degradation
  - DFA tanks Uninsulated
  - Rapid Cooling of DFA as it leaves the distillation still
  - Nitrogen blanketing
  - Citric Acid addition

Degradation of TFM by Biological Oxidation

Microbial organic growth in presence of **moisture**

Two mechanism proposed for this

β-Oxidation & ω-Oxidation

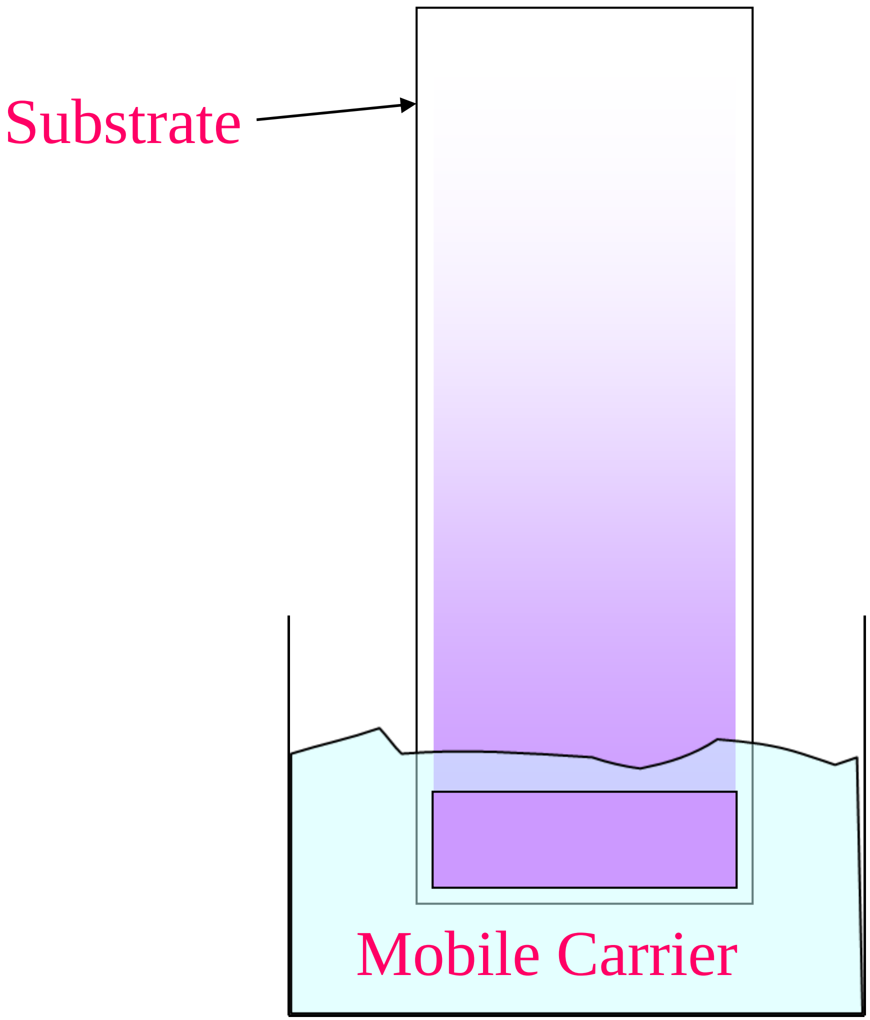
ω-Oxidation

- Terminal Carbon atom attacked by Microbes
- Dicarboxylic acids are formed and excreted e.g. Sebacic acids, suberic acid etc.
- Presence of other ketonic bodies has been observed leading to further complex biological degradation of oils

- Some of these compounds will get removed during distillation but some will co-distill : **Rancid Odors**

Role of Structurant and other inorganic materials

Chromatography Principle/Wicking effect of structurants



Explained by

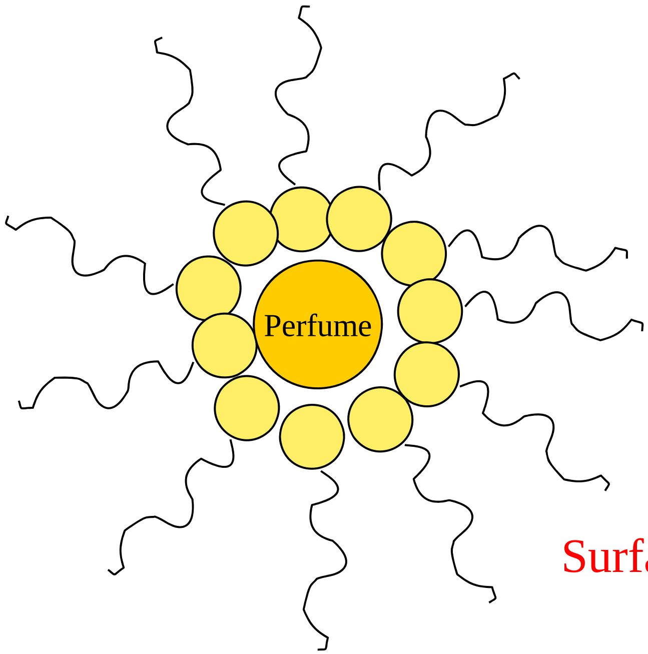
- Surface adsorption
- Relative solubility
- Surface Charge
- Functional Group interaction

Substate= Structurant
Mobile Carrier= Solvents/Moisture
Ink = Perfume

Chromatography Principle applied to Structurants

Substrate : inorganic fillers e.g. Talc or Frisis (Hydrated Magnesium Silicate) or Alumina Hydrate, Sodium Phosphate, salts etc.

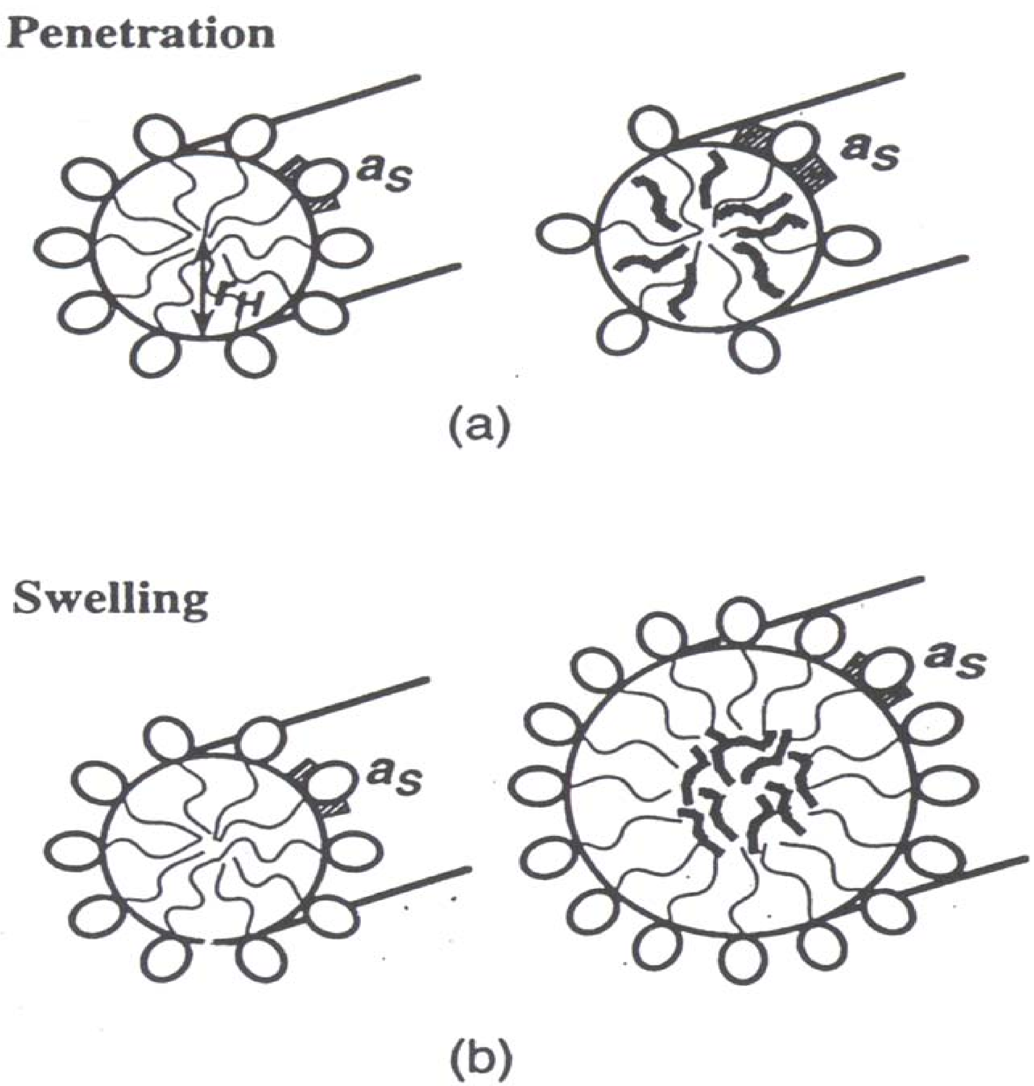
Organic molecules e.g. Glycerin, Surfactants



Surfactant Micelle

Organics also work by **solubilization** and **micellar & LC encapsulation**

Why is perfume delivery better from liquid soaps?



: surfactant molecule

: oil (perfume) molecule

Packaging: Chemical composition

- Stiffener : Virgin cellulosic material (Bamboo, Eucalyptus) extrusion coated with LDPE , Rosin as binder

- Outer wrapper :Agricultural Residue (AR:- Bagasse) recycled, Fungistat :Sodium Salicylanilide (SSA), China clay as binder

- Printing inks : Pigments + Solvents
    - Pigments : Phthalocyanine Blue, Yellow etc.Defined by a Colour Index number
    - Solvents : MEBK, MIBK, MEK, Toluene etc.

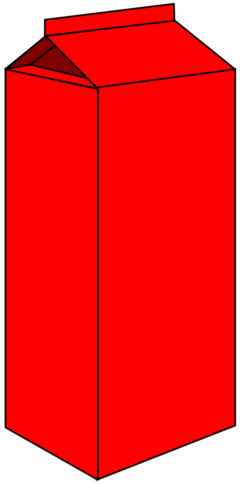
Outer Packaging

- Stiffener : Paper, resinuous gums, polymer coating, wax etc. In constant touch with the soap therefore interaction with residual Chlorine + Transition metals

- Outer wrapper : Paper + Printing Inks

- Printing inks : Aromatic compounds, phenols and resins along with solvent carrier.

- All have complex reactions with soap
- Metal content is specified and controlled



Q&A

- High TFM = Higher Quality of Soap ?
  - High TFM≠ Higher Quality e.g. Dove
  - Quality of TFM » Quantity
- Customers complaining of soap fragrance not lasting after a few bath? How is it connected to formulation?
  - Fragrance affected by base odor/ migration due to wicking/micellization
- What additives affect fragrance delivery ?
  - Inorganics like Soda/silicate affect greatly. Talc to some extent.Liquid crystal disruptors play a part in perfume delivery on skin (Patent EP0311343). Shielded Cationics/Shielded Starch Encap will work/Silicones/ MCT will also work
- Mixtures of oils= good formulation ? How to use cheaper oils ?
  - Cheaper oils can be used without impacting fragrance delivery by using a good formulator
  - Even if the oil is cheap Freshness counts! Fresher the oil for the soap base = better fragrance impact.

Q&A

- What shapes/colours/ textures/ designs are possible ?
  - Anything is possible. Moulded soaps give more freedom than extruded soaps (at higher costs)
- Can two sides of a soap have different fragrances?
  - Yes, Both extruded and moulded soaps
- What is Virgin base?
  - Non-recycled. Sometimes it also refers to soaps made from Oils and not Acid byproducts
- What is the best possible base available in India and the world?
  - 40 RBDPS/ 40 Palm Oil/20 CNO euivalent with C12 from CNO is the best possible base in the world. Available through the malaysian manufacturers (due to freshness of oil)
- What factors affect soap base costs?
  - Oil/Caustic/location of factory/scale of operation

Q&A

- What is Tallow soap? Why does it have odour?
  - Tallow is one of the oils from Beef production. It has its own unique odor due to presence of small amounts of proteins.
- Glycerine soaps and winter usage? Which soaps will dry the skin the least?
  - Non soaps like Dove. Less lather in the soaps more milder it will be
- Fairness soaps do they work ?
  - No all. Sunscreen soaps work but Fairness soaps don't at a consumer level.
- Can a shower gel give squeaky clean feel like soap ?
  - Yes.