Toilet Soaps and Bathing Bars

Soap you are aware is the alkali salt of a fatty acid with a general formula NaOOC(CH2)nCH3. Soap properties exists when (n+2) is greater than 8 and less than 20. The best properties occur when (n+2) equals 12 to 18. The fatty acids used to make soap are obtained from fats and oils. The fatty acids have varying chain lengths, which are all straight chain and contain even number of carbon atoms. There are about 40 different fatty acids occurring in nature, the largest is the group containing 18 carbon atoms.

Of the different fatty acids the most important with respect to soap manufacture are

Lauric Acid	12 Carbon Atoms
Myristic Acid	14 Carbon Atoms
Palmitic Acid	16 Carbon Atoms
Stearic Acid	18 : 0 Carbon Atoms
Oleic Acid	**18: 1 Carbon Atoms**
Linoleic Acid	**18: 2 Carbon Atoms**
Linolenic Acid	**18: 3 Carbon Atoms**
Ricinoleic Acid	**18 : 1 Carbon Atoms**

The last four fatty acids in bold letters, are unsaturated fatty acids. Unsaturated fatty acids gives softer soap with lower melting point and is less stable.

Hard fats like, Mutton tallow, beef tallow, Lard and Palm oil contain longer chain saturated fatty acids and soaps made from these fats are firm, slowly soluble, milder and have a good detergency.

Lauric Oils like Coconut Oils, Palm Kernel Oils, have shorter chain fatty acids which form soap that give faster tighter more copious lather which are less mild than soap from hard fats.

Soft Oils like Groundnut Oils, Cotton seed Oils, Rice Barn Oils, contains more unsaturated fatty acids. Soaps made from these oils are softer less white and less stable

Soft Oils are hardened by catalytic hydrogenation and bleached to improve the properties of soap. There is usually a loss of natural antioxidants found in the oil during the process of bleaching and hydrogenation. Antioxidants may be necessary to prevent rancidity developing in the oils and soaps made out of these oils. Excess Linoleic Acid and Linolenic Acid in soap oil blend is not advisable as they develop rancidity faster.

It is seen that a judicious blend of oils and fats are necessary to obtain soap with ideal properties. It is also necessary to blend different oils for economic reasons. Blend are so adjusted to control hardness, plasticity, lather, mush, cracking, mildness and discoloration.

The following are some of the major vegetable oils used in India for soap making. The table lists the fatty acid constituents and their percentage in these oils.

Oils Fatty Acids	Coconut Oil	Mowrah	Rice Barn Oil	Palm Oil	Castor Oil	Neem Oil	Groundnut Oil
Lauric $C_{12}H_{24}O_2$	48						
Myristic $C_{14}H_{28}O_2$	17. 3						
Palmitic $C_{16}H_{32}O_2$	8. 8	24	17	42. 5		14	7
Stearic $C_{18}H_{36}O_2$	2	19	2. 7	4	0. 3	19	5
Oleic $C_{18}H_{34}O_2$	6	43	45	43	8. 2	49	60
Linoleic $C_{18}H_{32}O_2$	2. 5	14	27. 7	9. 5	3. 6	16	21
Linolenic $C_{18}H_{30}O_2$							
Ricinoleic $C_{18}H_{34}O_3$					87. 6		
Iodine Value	10	62 to 70	92 to 109	50	85	69 to 72	90
Sap Value	252 to 260	188 to 192	183 to 194	196 to 206	177 to 187	190 to 204	189 to 193
Titer C	20 to 23	38 to 42	26.9	38 to 47	3	35 to 36	28 to 32

Total Fatty Matter is historically considered a beneficial ingredient in Toilet soap. Acute Shortage of Oils and Fats in India led to Research by (HLL) Hindustan Lever Limited (Unilever India) to create low TFM soaps that performed at par with High TFM Soaps. These Low TFM Soaps were also termed as Bathing Bars or Structured Toilet Soaps

We know that the properties of soap depend on the following parameters.

- The chain length of fatty acids in blend
- Amount of saturation and unsaturation (Double bond in the structure)
- Formulation
- Soap Structure

Soap consists of Solid crystals in a continuous liquid crystalline matrix. The solid crystals represent the "bricks" and the liquid crystalline matrix represents the "motor." The particulate size is in the micron range.

"Bricks" - "Insoluble Soaps" are responsible for Bar Hardness, Lather Stability, and facilitate in easy processing

“Motor” - “Soluble Soaps” are responsible for Lather Volume, Detergency / Cleaning, Perfume Carrier and perfume retention.

Solubility of soaps made out of various fatty acids is related to the chain length as well as the extent of unsaturation.

- Short Saturated (CNO / PKO) - C8 - C14 Slightly Soluble
- Long Saturated C16 - C18 Insoluble
- Unsaturated C 18:1 Very Soluble
- Hydrogenated RBO / Tallow 50% Soluble + 50% Insoluble

All Soaps Ex Drier (as per X Ray Defraction studies) undergo Rapid solidification with non- -equilibrium crystals. The soap obtained consist of Sodium laurate + Sodium Stearate complex (Solid Component) and Sodium Oleate + Super Saturated Sodium Stearate + Sodium Laurate (Liquid component). The soap structure is brought to equilibrium by milling during which the Insoluble Solid Soap (Sodium Stearates and Sodium Palmitates) and the Highly soluble liquid Soap (Sodium Laurates / Sodium Oleates) are evenly distributed.

In short we can say that a 78 TFM soap contains

39 TFM – Soluble Soaps (Sodium Laurates and Sodium Oleates) and
39 TFM – Insoluble Soaps (Sodium Stearate and Sodium Palmitate)

Accordingly HLL contends that if 39 TFM - Insoluble Soaps (Sodium Stearate and Sodium Palmitate) in the formula is replaced with Starch, Talc, Kaolins, Phosphates, China Clay we get structured Soap or Bathing Bar or Low TFM Soap that has performance almost at par with toilet soaps. Moreover it saves valuable Vegetable Oil and prevents wastage of Sodium Laurates and Sodium Oleates Soaps that complexes with Sodium Stearates and Sodium Palmitates insoluble soaps during use. According to HLL, Consumer tests have proved that

- Low TFM Soap are at par with conventional 78 - 80 % TFM Soaps with respect to
- Lather and detergency
- Mildness to skin
- Good Perfume Retention
- Economical, Fat Charge manipulation in case of Oil shortage.

The only negative is that Fine Talc added to can affect sensitive eyes

Major Odours observed in Sodium Soaps of fatty acids (Vegetable Oils)

- Lauric Acid : Creamy, Fatty, Rancid
- Oleic Acid : Oily Green, animalic
- Stearic Acid : Almost Odourless
- Palmitic Acid: Dry, Chalk, Chemical?
- Recinolic : Peroxide odour
- Linoleic :Leafy, green, metallic, hydrogenated

In case of low TFM Sodium Soaps the odours of insoluble matter plays an important role.

- Cosmetic Talc: Almost Odourless.
- Kaolin : Chalky
- China Clay : Muddy, Earthy
- Starch : Carbohydrate odour if spoiled then foul decomposing odour

HLL principally uses Cosmetic Talc as filler. Talc is a naturally occurring mineral. Chemically it is Hydrated magnesium silicate; [$Mg_6Si_8O_{20}(OH)_4$]. Structurally talc is a layer-lattice mineral, composed of a brucite sheet $Mg_6(OH)_{12}$ sandwiched between sheets of silica. The electrically neutral layers are held together by weak Van der Waals forces. Cosmetic Grade Talc is prepared by milling from selected mines of very high quality and purity. Pure talc is white in colour with a slippery feel and good powers of oil absorption. It is inert to most chemical reagents and is very soft in nature having only a hardness of 1 on the Moh's hardness scale. Cosmetic Grade Talc when dispersed in water, it has an alkaline pH of 9 to 9.5. Talc used in should have a smooth feel with the talc particles passing through standard 200 mesh sieve and is not gritty.

Talc acts as a carrier for perfume. Perfume stability and its final impact in toilet soap mainly depend on the pH of talc used, and the heavy metal impurities present in it. Impurities of hard minerals like silica, quartz, adversely affect the smoothness of talc and so have to be eliminated. Mineral impurities such as quartz, chlorite, dolomite, magnesite, calcite, specks of mica and ultrabasic silicates having a chain silicate structure like amphiboles that include termolite, anthophyllite, actinolite, etc. should be absent. Carbonates such as dolomites, calcite, magnesite, and phosphates like apatites are other major contaminants in talc can also affect the perfume integrity due to their potential reactivity with perfumery ingredients.

We know that the fragrance used should mask base odour, enhance product appeal, and should be compatible with the base component. The fragrance used should be stable during the accelerated storage study to confirm the stability of the fragrance throughout the shelf life of the final products at varying environment. In case of bathing bars one should also consider the comparatively higher temperatures encountered during processing.

The physico chemical principles that govern stability of the fragrance in a Soap include

- Adsorption of Fragrance by Soap
- Evaporation of Fragrance
- Auto Oxidation of Soap and Fragrance
- Reactivity of fragrance due to the following equilibrium

$$RCOONa + H2O \leftrightarrow RCOOH + NaOH$$

Used in Soaps,

- some Fragrance will blend and remain in the aqueous phase,
- some of Fragrance will be adsorbed on the outer surface of the soap,
- some fragrance may be absorbed between the methyl tails and
- some fragrance will become oriented in the miscelle forming more or less stable complex.

The different classifications of soap, as per Indian laws as below. You will notice that soap cartons now mention Grade I, II or III.

As per BIS (Bureau of India Standards) Soap grades are as given below

Grade I	Minimum TFM 76%
Grade II	Minimum TFM 70%
Grade III	Minimum TFM 60%
Bathing Bar	**Minimum TFM 40%, Minimum Surfactant 4% (Mandatory)** **To pass Performance specifications of BIS**

Now can one generalise to say that all higher TFM soaps provide additional benefits over a lower TFM soap. The answer according to HLL study is NO.

If the Oil blend (20 Lauric Oils: 80 Other Oils) (In light of the above discussion) used is same then a higher TFM soap is better than the lower TFM soap. However Lauric Oils are expensive so manufacturers reduce the Lauric content in the oil blend, but keeping the Oil content in the total soap same. In this case, you get Toilet soap with higher TFM but with lower performance. In fact, even if the TFM content is lower the resultant soap will perform better if the Oil blend has a higher percentage of Lauric Oils.

As an example for better understanding let us, consider the following

Soap A : TFM 60%, Oil Blend approx. 20% Lauric Oils 80 % Other Oils.
Soap B : TFM 80%, Oil Blend approx. 10% Lauric Oils 90% Other Oils.
Soap C : TFM 70 %, Oil Blend approx. 10% Lauric Oils 90% Other Oils.

As per BIS regulation **Soap A is a Grade III** quality, **Soap B is a Grade I** and **Soap C is Grade II** quality. The gradation is done based on TFM.

In Actual practice **Soap A** will have better performance than Soap B or Soap C although it is a **Grade III soap with only 60% TFM.**

It is logical to question as to " Why would a soap maker spend more money to put a higher TFM soap on the market if there are no extra benefits over a low TFM soaps it does not make economic sense."

To answer, we can say that replacing TFM with Talc (Filler) is beneficial to the manufacturer as Talc is less, expensive compared to Oil (approx. Rs. 40 : Rs. 4). However, if the performance is to be bettered then the Lauric Oil content has to be increased. In spite of this increase in cost in the Oil blend, the manufacturer ends up in making good savings. This savings can then be used to improve the soap quality further by using a part of the savings to increase fragrance dosage, add antimicrobials TCC / TCS, Speciality additives, improve finish like pearlscent, better wrapper, better promotion in TV and press, etc. (HLL does exactly this. Another manufacturer sells only Grade I soap and still make substantial profits by reducing the Lauric Oil content in the Oil blend but gives higher TFM.

So is it right in saying that the Lauric content in soap is a major determinant of quality regardless of TFM content. If yes, then all manufacturers would prefer the "LUX" route of lower TFM but higher Lauric content and therefore a better quality soap (at a lower cost?).

HLL because of their muscle power and being a pioneer of this was able to carry out the technique better. Political lobbying also had a large role to play. In the early 90's Lauric, oils were not available due to poor agricultural output and so this theory worked. In the last 5 years, there has been a good monsoon and availability of Lauric oil has improved substantially in the country. The farmers lobby has been forcing the Government to reconsider use of Lauric oils for soap making so that they can profit. The Talc manufacturers (Rajasthan) lobby wants to continue use of Talc in soap. In fact, most Indian soap manufacturers in India following the footsteps of HLL used talc at one time or the other to make soaps but were not very successful.

Godrej the only manufacturer of AOS (α - Olefin Sulphonate – Surfactant) has joined the fray, insisting on using 4% AOS in bathing bar and to some extent they have succeeded in getting a bathing bar spec according to their requirements.

To the chagrin of all HLL have increased their TFM content to 60 % TFM from the earlier 50 % TFM and are marketing their soap as Grade III. This helps them not buy AOS from Godrej (HLL's competitor in the Soap business) in substantial amounts as they do not make bathing bar and Grade III soap do not require AOS.

Economics is favourable if one can get Lauric oils at lower prices. This is possible for big players. HLL makes substantial profits using this route and uses the savings for promotions on TV and Press. This pushes volume/sales further making more profits and better bargaining power with the Lauric oil dealers. In short, it is a win - win situation for HLL.

Other determinants for soap quality will definitely be a good fragrance, better packing, good looks, speciality additives, herbal additives etc.