

Laundry Detergents — Moving from Solid to Liquid

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If we look through the world laundry detergent market, we will not fail to observe that the changes taken place are very much significant in the last decade. During this period, consumer usage habits have changed from using simple detergent powder to concentrated powders, detergent tablets, detergent pastes, detergent gels and so also liquid products. In spite of all these changes taking place in the developed world, laundry soaps, synthetic detergent bars/cakes and powder continue to be popular in the Indian subcontinent. Local economics, consumer need, government regulations, safety and ecological requirements, raw material and water availability, technology and most importantly the cost incurred on formulating have a major influence on the popularity of product forms.

Consumer needs vary depending on habits or practices, and the value a consumer attaches to the product at that price. While formulating a detergent product, one should most importantly consider the market dynamics, as only this will give an indication whether the product will be accepted or not by the consumer. Other considerations that will determine product success or failure include: government regulation (past, present and future), the size of the market, the cost and availability of raw materials, packaging materials and machinery. Similarly, formulation technology should consider product related aspects like ingredients, their performance, safety in use and manufacture, the method of manufacture, stability of the product (with reference to the normal shelf life), and aesthetics. Most importantly, the technology used should be able to blend with the market dynamics.

Laundry soaps

India has a high consumption of laundry hard soap. Laundry soaps are produced by saponification of non-edible fats and oils largely depending on the availability. Soap is produced by several methods right from the old kettle system to continuous saponification methods. The final product

either can be a pure soap (unfilled soap) or with additives added (filled soap). The quality of the soap obtained depends on the quality of the oils and fats utilised in making the soap fat blend. Poor quality fats and highly saturated oils give poor quality soap. Coconut Oil, Rice bran oil, Castor oil, Neem oil, Mowrah oil, Palm kernel oil, Palm Oil, Palm fatty acid distillate, Acid oils, and other non-edible grades of oil are normally used for making laundry soap. Filled soap formulations contain additives like soda ash, clay, silicates in addition to colour pigments, and fragrance. Wet soaps are blended with the required ingredient in an amalgamator or sigma mixer and then extruded in form of billets for stamping and packing. Normally, laundry soaps contain 20 to 30% moisture and TFM is around 45 to 50%. India is a hand wash market. Filled and unfilled laundry soaps offer good cleaning at low cost. However, laundry soaps perform poorly in hard water areas.

Detergent bars

Synthetic detergent bars are an efficient alternative to laundry soap. They have good foaming and cleaning activity similar to soap but without its disadvantage of non-performance in hard water. Synthetic detergents also have additives and other auxiliary speciality chemicals that greatly enhance the performance in comparison to laundry soap. The basic active ingredient is an anionic detergent, Linear alkyl benzene sulphonate (LABS) or Acid slurry. LABS is not affected by the calcium and magnesium ions in hard water. Syndet bars are normally low cost formulations filled with mineral additives like clay, calcite and dolomite, maize starch, sodium sulphate and other speciality chemicals. LABS normally produce a soft bar difficult to extrude in a plant. To reduce the softness, hardening ingredients like zeolites, phosphates, silicates, calcium and magnesium carbonates, aluminium and magnesium sulphate are used. The use of moisture is kept under limits to improve hardness and obtain a correct consistency. It is necessary that ingredients be added in a correct order as specified.

Detergent powders

Powder detergents are manufactured by the conventional spray drying method. In this method various heat substantive ingredients are mixed in a crutcher to a solid content of around 60 to 70% and the slurry sprayed dried to remove excess moisture to obtain a spray dried powder. Several factors are responsible to get the characteristic detergent powder type of required density, moisture and particle size. Formulation details, slurry solids content, slurry viscosity, spray drying temperature, pressure, tower height and design, spray nozzle type and angle in which it is placed, are all important factors to obtain a powder of required specifications. Fragrances, enzymes, bleaches, and bleach activators are all post dosed and blended in the spray-dried powder obtained to complete the formulation. Installing a spray drying plant is an expensive proposition. Apart from a large capital costs, energy and maintenance costs are also substantial. Spray dried powder is a low bulk density product that requires a larger package, increasing packaging costs. The other limitation is that heat sensitive materials have to be post-dosed later after the spray drying is complete.

Dry mixing is a cost-effective method to make a detergent powder. Most of the ingredients used in the manufacture of detergent powder are solids with the exception of the active surfactant namely LABS, which is a viscous liquid. The stickiness obtained due to the slurry is substantially reduced by use of light soda ash as a neutralising agent instead of Caustic alkali. Light soda ash also has the ability to absorb free moisture and thereby making the product free flowing. Another alternative is to optimise the level of acid slurry in the formulation so that there is no stickiness. The mixing of various ingredients is carried out either manually or by use of a simple mixer. Excess use of soda ash is normally done in this method. Soda ash performs the function of neutralising, besides the functions of water softening and maintaining the pH of the wash liquor. Other additives are then added one after another to complete the batch. Although lower capital cost and energy is required to prepare dry mix detergent powder (when compared to spray dried method) there is much less control over product density and particle size. The non-uniform size of particles therefore makes the powder dissolve more

slowly, unlike in a spray dried product where the product is in the form of hollow beads that dissolve very rapidly in water at all temperatures. The advantages of concentrated dry mix powder far outweigh the disadvantages and it has gained consumer acceptance. As concentrated dry mix powders have much lower diluent, they are perceived to be more ecologically acceptable.

Compact detergents

Compact detergent powders are another detergent product form. It is concentrated almost four times the strength of a conventional powder and so has enhanced detergency. The advantage here is to use a much lesser quantity of the powder per wash. The technology used to prepare the compact is a combination of spray drying and agglomeration. Agglomeration is defined as particle size enlargement. Sticking together of smaller particles to form larger units is the typical process. Changing particle size is one of the important reasons of agglomeration. It improves the flow characteristics and helps in easy dissolution of the powder in the wash water. Agglomerates are not dusty, and easy to handle, making it user friendly and environmentally safe. Chances of certain ingredients settling at the bottom of a pack is avoided, as by agglomeration a uniform distribution of the ingredients is possible in the final product. Agglomerates are made by using a spray drier in combination with an agglomerator.

Detergent pastes

Laundry pastes are manufactured by mixing all the ingredients in a crutcher, where neutralisation reaction between the acid slurry and the alkali takes place *in situ*. The crutcher is designed to avoid aeration of the product during manufacture. The semi-solid mass is then stored in a suitable tank and then packed for dispatch.

Detergent tablets

Detergent tablets are claimed to be another revolution in the use of laundry detergent industry in the last decade. Tablets claim to provide not only a great cleaning, but also makes washing less tedious, offering good value for money. The biggest advantage in case of tablets is that there is no need to measure out the amount of powder during wash

thereby preventing unnecessary wastage. Tablets are placed in a specially designed net that helps the tablet to disperse gently and evenly throughout the washing cycle. Laundry detergent tablets have compositions very similar to concentrated powders, having surfactants, builders, bleaches, enzymes, and fluorescent whitening agents. Compressing and compacting a premixed basic detergent powder formulation in a high-pressure press die produces detergent tablets. The use of binders assists in compression by allowing lower compaction pressure. It is important that tablets should have sufficient strength when dry, but at the same time is soft enough to disperse and dissolve in water — neither too quickly or slowly. Detergent tablets can also be made up of two layers. This format also allows separate incorporation of chemically incompatible ingredients in different layers and combining them into a single tablet. Making twin layer tablets is without doubt more difficult as now it has two base powders and two pressing steps. Consumers today look for effective and easy-to-use products. Laundry bars, detergent cake, pastes, and powders all have their advantages and disadvantages. Using laundry bars, detergent cake, pastes involves various steps, making the entire washing process difficult and time consuming. In case of detergent powders, dispersion and dissolution in the wash water is a concern.

Advantages and disadvantages of liquid detergents

With the increase in the urbanisation of population, continuous media coverage, influence of advertising, rising education, standard of living, and higher disposable income, consumer requirements change. Consequently, newer product forms and superior formulations become necessary to satisfy consumer requirements. Liquid detergents are becoming popular around the world due to its convenience in dispensing, easy dispersion and dissolution in the wash water. When the first liquid detergent were introduced it consisted only of 5 to 20% anionic surfactant dissolved in water. They became popular as they gave a better performance than the available soap and detergent powders, especially when used for dish washing and for laundering delicate fabrics like silk, wool and synthetic fabrics. These products have now evolved into more sophisticated products containing builders and aux-

iliary speciality chemical ingredients. The biggest advantage with liquid detergents is from the manufacture point of view. Liquid detergents can be made by use of simple inexpensive equipment, unlike in case of detergent cakes, powder, compacts, pastes and tablets that all require relatively more sophisticated plant equipment and operating conditions. In case of detergent powder and bars, fillers are necessary to dilute the product to make it cost effective and economical. In case of liquid detergents, the diluent is simply water that is cheaper to obtain and to use. A simple stainless steel vessel with a slow speed stirrer is adequate to make liquid detergents. It is important that the stirrer is attached in a manner that will not cause foaming during manufacture. The manufacture of liquid detergent is suitable for small-scale industrial units and small manufacturers. Manufacturing liquid detergents involves only a simple mixing process that can also be carried out manually with a wooden ladle or by using a simple electrical stirrer. Ideally, a liquid detergent should incorporate all ingredients normally found in a conventional powder so that equivalent washing performance is achieved. However, this is not easy, as the formulator has to overcome some basic problems. One is the need to soften water for better detergency, increase the solubility of the detergent, and at the same time preserve the stability of bleaching agents in an aqueous base.

Categories of liquid detergents

Major categories of liquid detergents are: Washing up liquids/Dish washing liquid detergents; Light-duty laundry liquid detergents; and heavy-duty laundry liquid detergents.

Washing up liquids/Dish washing liquid detergents

Washing up liquids are used mainly to wash soiled dishes and cooking utensils in the kitchen. Washing up liquids are a blend of primary surfactants with additives that include viscosity modifiers, fragrance, preservatives, UV absorbers, colour, etc. Soiled dishes normally have mixed oils, fats, starches, cellulose, protein, etc. A good cleaning and emulsifying performance is necessary to make the washed dishes and kitchen utensils free from soil streaks and stains. As the utensils are cleaned the concentration of the soil in the liquid

detergent used keeps increasing. The detergent used should be able to provide a good supply of foam. Foam distributes the soil particles evenly and at the same time emulsifies the fatty soils in the substrate. It is important that good lather is maintained until the end of the washing process as the article is washed out clean and neat. The primary surfactant used in washing up liquid formulation includes Linear alkyl benzene sulphonate (LABS), neutralised with sodium, ammonium, and magnesium hydroxide or sometimes with triethanolamine. Although these are good emulsifiers, they are sensitive to water hardness. Linear alkyl benzene sulphonate obtained by sulphonation of LAB with sulphur trioxide gas contains minimum free sulphuric acid and is preferred to LABS obtained from oleum sulphonation that has a higher proportion of free sulphuric acid. Free sulphuric acid present precipitates as sodium sulphate increasing the inorganic content of the product and thereby reducing the cloud point of the final product. LABS based surfactant need solubilisers so that they become soluble at low temperature. Alkyl ether sulphates (AES) are added with LABS compounds so that an opaque and a cloudy product is not obtained, specially on low temperature storage. AES possess high surface activity. It also improves foam appearance and profile in presence of calcium and magnesium ions present in hard water. AES gives a better feel to the wash liquor and improves mildness of the product. Some primary surfactants are paraffin sulphonate, Alpha Olefin Sulphonate (AOS), Secondary alcohol sulphates, Alkyl polyglycosides (APG).

Secondary surfactants are normally used at lower concentration levels than primary surfactants. These are normally non-ionic surfactants and include products like Alkyl Ethoxylates, Alkyl Monoethanolamides, Diethanolamides, and Amine Oxides. Secondary surfactants improve foam generation and help in making the product thicker. Amphoteric surfactants like betaines can also be used as secondary surfactants for making premium products for foam generation and making the product milder. Once the choice and the level of surfactant are finalised, hydrotopes are added to ensure stability under all storage conditions. Hydrotopes also maintain transparency during storage and use over a range of temperatures. Sodium toluene sulphonate, Sodium xy-

lene sulphonate, urea, ethyl alcohol, propylene glycol, triethanolamine, either in combination or singly, are used as hydrotopes, in high active formulations that have a tendency to become cloudy. Hydrotopes or solubilisers reduce the viscosity of the formulation. Hydrotopes thus act counter to secondary surfactants. In low cost formulations, sodium chloride, sodium sulphate, or cellulose based thickening agents are also used to increase viscosity, in place of additional secondary surfactant usage. Foam in any formulation is optimised by judicious use of primary surfactant and secondary surfactants. Washing up liquid is normally marketed as a coloured, transparent, liquid detergent, but sometimes also as an opaque liquid, purely for marketing reasons. The most common fragrance profiles in wash up liquid detergents are lemon, citrus, or mild floral. One important requirement regarding fragrance used is that it should not be substantive or retain in the washed kitchen articles. A typical wash up liquid formula may look like this:

LABS	18 to 20 %
SLES	05 to 08 %
Cocodiethanol amide	1.5 to 3.0%
Ethanol	3.0 to 4.0 %
Preservative	0.2 %
Sodium chloride	0.2 to 0.5 %
Colour	as required
Fragrance	0.2 to 0.3 %
Water	to 100

Light duty laundry liquid detergent

Light duty liquid detergents are used for washing delicate fabrics, like wool, silk, and synthetics. Light duty liquid detergents evolved from washing up liquid detergent formulations that are made by use of more expensive raw materials. Light duty liquid detergents have a very similar formula as washing up liquid detergent when intended for a hand wash product. However, the emphasis is more on the fabric cleaning ability. It is important that light duty liquid detergents are easily dispersed in water are mild and gentle to hands and the fabric washed. The pH is neutral or very slightly alkaline. Light duty liquid detergents normally do not contain builders or bleaches. This loss of detergency and performance is compensated by a higher use of speciality ingredients like fluorescent whitening

agents, etc. Light duty liquid detergents are normally based on Alkyl benzene sulphonic acids, Alcohol sulphates, non-ionic, sulphated non-ionic or amphoteric surfactants. Surfactant actives can be used either singly or in combination. Sometimes soaps also form a part of the formulation. A blend of surfactants is preferred as it improves the ability of the product to clean different types of clothes and remove soil. It also makes the product milder to the fabrics washed and to the users skin. It is to be noted that ethylene oxide condensation type surfactants, when used, forms a cloudy solution at higher temperature and is clearer at lower temperature conditions. It is essential that all products be tested for this aspect, as clouding can take place during the shelf life of the product.

Combining cationic and non-ionic surfactants we can obtain a product having softening, conditioning and anti-static properties suitable for fine wash products. We can also use mild cationic polymer resins in place of cationic surfactants to avoid the problem of cationic surfactant build up. We know that cationic build up on delicate fabric leads to rapid re-soiling and yellowing of fabric. A substantive fragrance (dosage 0.15 to 0.4%) is an effective indication to the consumer of fabric care and conditioning. Chelating agents, viscosity modifiers, pearling agents, colour preservatives are other ingredients added to complete the formulation. Enzymes are normally not added in hand wash product forms. Fine fabric laundry liquid detergents range from the low-priced, to the premium and expensive. Opacifying agents like aqueous dispersion of an alkali insoluble polymer of styrene, substituted styrene, copolymer styrene derivatives with acrylamine, Polyvinylidene chloride, etc are all used in LABS based formula to give an opacifying effect for enhancing the aesthetics of the product for marketing claims.

Light duty liquid detergent formula can be just a simple dilute solution of cationic surfactant to the expensive complex formula containing surfactant blends and speciality additives. The final product can be pearled, a fabric shampoo with conditioning properties, skin friendly and mild. LABS in a premium product can be replaced by other anionic like paraffin sulphonate, fatty alcohol sulphate, fatty

alcohol ether sulphate, etc. Nowadays AOS that has a good fabric softening effect on wool, silk and acrylics is also very popular in place of LABS. Detergents containing non-ionic like ethoxylated fatty alcohol, alkyl polyglucosamide and methyl ester sulphonate is also very popular.

Heavy-duty liquid detergents

Heavy-duty liquid detergents are distinctive because of their relatively high surfactant level, sometimes even up to 40%. However, due to stability and solubility problems, most of the products in the market do not contain builders or bleaching agents. Heavy-duty liquid detergents are effective in removing grease and greasy soil at wash temperatures below 60 degrees centigrade at much lower dosage levels. The cleaning ability naturally depends on the water hardness and the amount of the soil in the substrate.

Heavy-duty liquid detergents involves a sound formulation technique, as liquid active matter, sequestering agents, silicates, anti redepositing agents, florescent whitening agents, etc., all need to be formulated in the product and yet a clear liquid with a low cloud point is to be obtained. It is important that utmost care is taken while formulating, otherwise there are chances of the product separating into two phases with each one having a different proportion of ingredient concentrations. Heavy-duty liquid detergents are of two types. Structured variety with inorganic builder incorporated and an unstructured variety without any inorganic builder. In the structured liquid type, the muscular configuration of the active ingredients is viscous enough to support the inorganic builder. The products are white opaque or pastel in colour due to the inorganic builder particles in it. In case of unstructured heavy-duty liquid detergents, oil soap, and a synthetic wash active mix is used in place of inorganic builders. In hard water conditions the soap reacts with the calcium and magnesium ions and forms a scum that remain in solution due to the high level of anionic and nonionic surfactants in the wash liquor. Liquid formulation is light sensitive and would require UV absorbers, especially when packed in a transparent bottle. In the absence of UV absorbers in the formulation, it should be dispensed in an opaque container.

TABLE 1
SOME TYPICAL EXAMPLES OF LIGHT DUTY LIQUID DETERGENTS

Ingredient	%	%	%
LABS	17.6	10	
SLES	6.5		
Lauryl alcohol ethoxylate	1.5		22
Florescent whitening agents	0.1	0.1	0.1
Sodium chloride	0.3		
AOS		2.2	
Fatty Alcohol Ether sulphate			1.7
Lauric Soap			2.2
Triethanolamine		2	
Caustic Alkali 45%		1.8	
Ethanol	7		
Preservatives	0.2	0.2	0.2
Cocodiethanolamide		11	
Polymer Antistat / Poly quart			2.2
Colour	As required	As required	As required
Fragrance	0.3	0.3	0.3
Water	To 100	To 100	To 100

TABLE 2
TYPICAL FORMULAS OF STRUCTURED AND SOAP SURFACTANT BASED HEAVY-DUTY LIQUID DETERGENTS

	Structured	Structured	Unstructured Soap Synthetic	Unstructured Soap Synthetic
Anionic Surfactants	5 – 7	12	12 – 18	6 – 10
Non-ionic Surfactant	1 – 3		13 – 19	
Alkyl ethoxylate		13		1 – 3
SLES		3.2		
Cocodiethanolamide				0.5 – 2
Coconut fatty acid		12		
Sodium / Potassium Soap	1 – 2			0 – 2
Triethanolamine		8		
Caustic Alkali		1.7		
Solvent / Alcohol	0.5 – 2.0	10		0 – 5
Lauric Soap neutralised with Triethanolamine			12 – 18	
Hydrotopes			5 – 10	
Builder	20 – 30			15 – 30
Silicate	0 – 1.5			1.5 – 3
Anti re-deposition agent	0.5 – 1		0.5 – 1	0.5 – 1.5
Fluorescent whitening agents	0.1 – 0.3	0.1 – 0.3	0.1 – 0.3	0.1 – 0.3
Enzymes	0.5 – 1	0.5 – 1	0.5 – 1	0.5 – 1
Fragrance	0.25 – 0.5	0.25 – 0.5	0.25 – 0.5	0.25 – 0.5
Water	Upto 100	Upto 100	Upto 100	Upto 100

In spite of many advantages in liquid detergents the main problem is the difficulty in incorporating bleaches and bleach activators. Naturally, the performance of liquid detergents in the removal of stubborn stains gets impacted in comparison to powders and bars. Manufacturers have tried to develop a water-free liquid formulation containing bleaches and bleach activators. However only minor success has been achieved as this poses problems of

stability, ingredient choice and in manufacturing. It is possible all these issues would be solved by the end of this decade and a stable formulation containing bleaches, organic builders and polymers, in place of phosphates, will be developed. If this is achieved then liquid detergent products will be concentrated, perform well, have soft, milder properties, and be consumer friendly and environmentally safe.