

## LIQUID DETERGENTS

*Excerpted from the paper published in Chemical Weekly, August 12, 2003, "Laundry Detergents – Moving from Solids to Liquids" by Sitaram Dixit, Senior Manager – Fragrance Applications, International Flavours & Fragrances India Limited*

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.

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 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 powder, 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 auxiliary 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's 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. Using a simple stainless steel vessel with a slow speed stirrer one can 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 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 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 all the same preserve the stability of bleaching agents in aqueous base.

**Major categories of liquid detergents are**

- ◆ **Washing up liquids / Dishwashing liquid detergents.**
- ◆ **Light duty laundry liquid detergents.**
- ◆ **Heavy-duty laundry liquid detergents.**

### **WASHING UP LIQUIDS / DISHWASHING LIQUID DETERGENTS.**

Washing up liquids is used mainly to wash soiled dishes and cooking utensils in the kitchen. Washing up liquids is 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 so that 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 triethanol amine. Although these are good emulsifiers they are sensitive to water hardness. Linear alkyl benzene sulphonate obtained

by sulphonation of LABS 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 are not obtained specially at 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 poly glycosides (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 Monoethanol amides, 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 xylene sulphonate, Urea, Ethyl alcohol, Propylene glycol, Triethanolamine, either in combination or singly used and a hydrotopes, in high active formulations, that has a tendency to become cloudy. Hydrotopes or solubilisers reduce the viscosity of the formulation. Hydrotopes thus act counter to secondary surfactants. In low cost formulation 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 looks 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 Florescent 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 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 anionic 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 sulphate, 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. Non-ionics like ethoxylated fatty alcohol, alkyl polyglucosamide and methyl ester sulphate is also very popular.

**Some typical examples of light duty liquid detergents.**

	%	%	%
<b>LABS</b>	<b>17.6</b>	<b>10</b>	
<b>SLES</b>	<b>6.5</b>		
<b>Lauryl alcohol ethoxylate</b>	<b>1.5</b>		<b>22</b>
<b>Florescent Whitening Agents</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>
<b>Sodium Chloride</b>	<b>0.3</b>		
<b>AOS</b>		<b>2.2</b>	
<b>Fatty Alcohol Ether sulphate</b>			<b>1.7</b>
<b>Lauric Soap</b>			<b>2.2</b>
<b>Tri Ethanol Amine</b>		<b>2</b>	
<b>Caustic Alkali 45%</b>		<b>1.8</b>	
<b>Ethanol</b>	<b>7</b>		
<b>Preservatives</b>	<b>0.2</b>	<b>0.2</b>	<b>0.2</b>
<b>Cocodiethanolamide</b>		<b>11</b>	
<b>Polymer Antistat / Poly quart</b>			<b>2.2</b>
<b>Colour</b>	<b>As required</b>	<b>As required</b>	<b>As required</b>
<b>Fragrance</b>	<b>0.3</b>	<b>0.3</b>	<b>0.3</b>
<b>Water</b>	<b>To 100</b>	<b>To 100</b>	<b>To 100</b>

**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 obtain clear liquid with a low cloud point. 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 non ionic surfactants in the wash liquor. Liquid formulation is light sensitive and would require UV absorbers specially when packed in a transparent bottle. In the absence of UV absorbers in the formulation, it should be dispensed in an opaque container.

**TYPICAL FORMULAS OF STRUCTURED AND SOAP SURFACTANT BASED HEAVY-DUTY LIQUID DETERGENTS.**

Ingredients	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

Inspite 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.