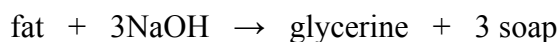


SOAP AND DETERGENT MANUFACTURE

Soaps and detergents are widely used in our society. Soaps are the product of the reaction between a fat and sodium hydroxide:



Soap is produced industrially in four basic steps. This article lists different steps because in the industrial processes described each of these is done over several process steps, but in principle it could be done in the three steps outlined here.

Step 1 - Saponification

A mixture of tallow (animal fat) and coconut oil is mixed with sodium hydroxide and heated. The soap produced is the salt of a long chain carboxylic acid.

Step 2 - Glycerine removal

Glycerine is more valuable than soap, so most of it is removed. Some is left in the soap to help make it soft and smooth. Soap is not very soluble in salt water, whereas glycerine is, so salt is added to the wet soap causing it to separate out into soap and glycerine in salt water.

Step 3 - Soap purification

Any remaining sodium hydroxide is neutralised with a weak acid such as citric acid and two thirds of the remaining water removed.

Step 4 - Finishing

Additives such as preservatives, colour and perfume are added and mixed in with the soap and it is shaped into bars for sale.

Detergents are similar in structure and function to soap, and for most uses they are more efficient than soap and so are more commonly used. In addition to the actual 'detergent' molecule, detergents usually incorporate a variety of other ingredients that act as water softeners, free-flowing agents etc.

INTRODUCTION

Soap is integral to our society today, and we find it hard to imagine a time when people were kept sweet-smelling by the action of perfume rather than soap. However, the current widespread use of soap is only a very recent occurrence, despite the fact that it has been made for more than 2500 years. The first recorded manufacture of soap was in 600BC, when Pliny the Elder described its manufacture by the Phoenicians from goats tallow and ash, and it was known among the British Celts and throughout the Roman Empire. However, these people used their soap medicinally, and it was not until the second century AD that it was used for cleaning, and not until the nineteenth century that it began to be commonly used in the Western world.

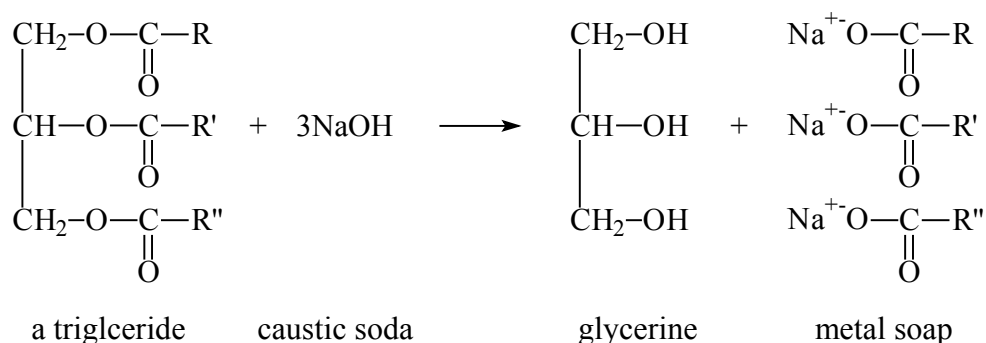
Early this century the first synthetic detergents were manufactured, and these have now taken the place of soap for many applications. Their manufacture is covered briefly in the second part of this article.

The Chemistry of Soap and Detergent Function

All soaps and detergents contain a surfactant¹ as their active ingredient. This is an ionic species consisting of a long, linear, non-polar 'tail' with a cationic or anionic 'head' and a counter ion. The tail is water insoluble and the head is water soluble - a difference in solubility which has two important implications. Firstly, this makes the surfactant molecule a wetting agent: the tails migrate to align themselves with the solid:water interface, lowering the surface tension at that point so that it penetrates the fabric better. Secondly, it allows the oily dirt particles to form an emulsion with the water: the tails of many surfactant molecules surround an oily dirt particle, forming a micelle with a drop of oil in the centre and the ionic heads of the surfactant molecules pointing outwards and hence keeping the micelle in the polar solution.

THE SOAP MANUFACTURING PROCESS

The essence of soap production is the saponification reaction:



This reaction is exothermic, and progresses quickly and efficiently at around 125°C inside an autoclave type reactor.

The most common fats and oils used are tallow (beef or mutton/beef blend), coconut oil, and palm kernel oil (**Table 1**). Different oils produce soaps of varying hardness, odour and lathering, so the ratios of the oils used are closely monitored to produce a blend with the most desirable characteristics for the most reasonable cost.

However, pure soap is hard and easily oxidised, so various additives are added to correct this and to make a more aesthetically pleasing product. The first such "additive" is glycerine, which is produced in the saponification reaction. Glycerine makes the soap smoother and softer than pure soap. However, it is also much more valuable than soap itself, so only a minimum of glycerine is left in the soap and the remainder is extracted, purified and sold.

The glycerine is extracted from the soap with lye² - a brine solution that is added to the soap at the saponification stage. Wet soap is soluble in weak brine, but separates out as the electrolyte concentration increases. Glycerine, on the other hand, is highly soluble in brine. Wet soap thus has quite a low electrolyte concentration and is about 30% water (which makes it easily pumpable at 70°C). To remove the glycerine, more electrolyte is added,

¹Surface active agent

²Pronounced "lee" in the UK and New Zealand and "lie" in the US.

causing the the wet soap to separate into two layers: crude soap and a brine/glycerine mixture known as spent lye, neutral lye or sweet waters. The soap still contains some salt, which itself functions as an additive, altering the viscosity and colour of the soap.

Table 1 - Fatty acids present in oil

	Tallow	Coconut oil	Palm kernel oil
lauric acid (dodecanoic acid - C ₁₂ H ₂₄ O ₂)		☐	
myristic acid (tetradecanoic acid - C ₁₄ H ₂₈ O ₂)	☐	☐	
palmitic acid (hexadecanoic acid - C ₁₆ H ₃₂ O ₂)	☐	☐	☐
stearic acid (octadecanoic acid - C ₁₈ H ₃₆ O ₂)	☐	☐	☐
oleic acid (9-octadecenoic acid - C ₁₈ H ₃₄ O ₂)	☐		
linoleic acid (9,12-octadecadienoic acid - C ₁₈ H ₃₂ O ₂)	☐		☐

Once the spent lye has been removed the soap is dried, chipped, mixed with other additives such as perfumes and preservatives and then plodded (squeezed together), formed into tablets and packaged for sale.

There are two different soap-making processes used in New Zealand, and these are both described below.

The Colgate-Palmolive Process

This is a continuous process (**Figure 1**) which uses a plant built by Binacchi & Co. The process is best understood in terms of two streams: soap flowing in the order given below against a counter-current of lye.

Step 1 - Saponification

The raw materials are continually fed into a reactor in fixed proportions. Assuming a production rate of 1000 kg wet soap per hour and a 80:20 tallow:coconut oil mix, the raw materials would be fed in at the following rates:

coconut oil	525.9 kg hr ⁻¹
tallow	131.5 kg hr ⁻¹
50% NaOH solution	³ 101 kg hr ⁻¹

³Although this is not the formula quantity, it gives a general indication to the process condition. The actual amount is affected by the caustic concentration in half - spent lye.

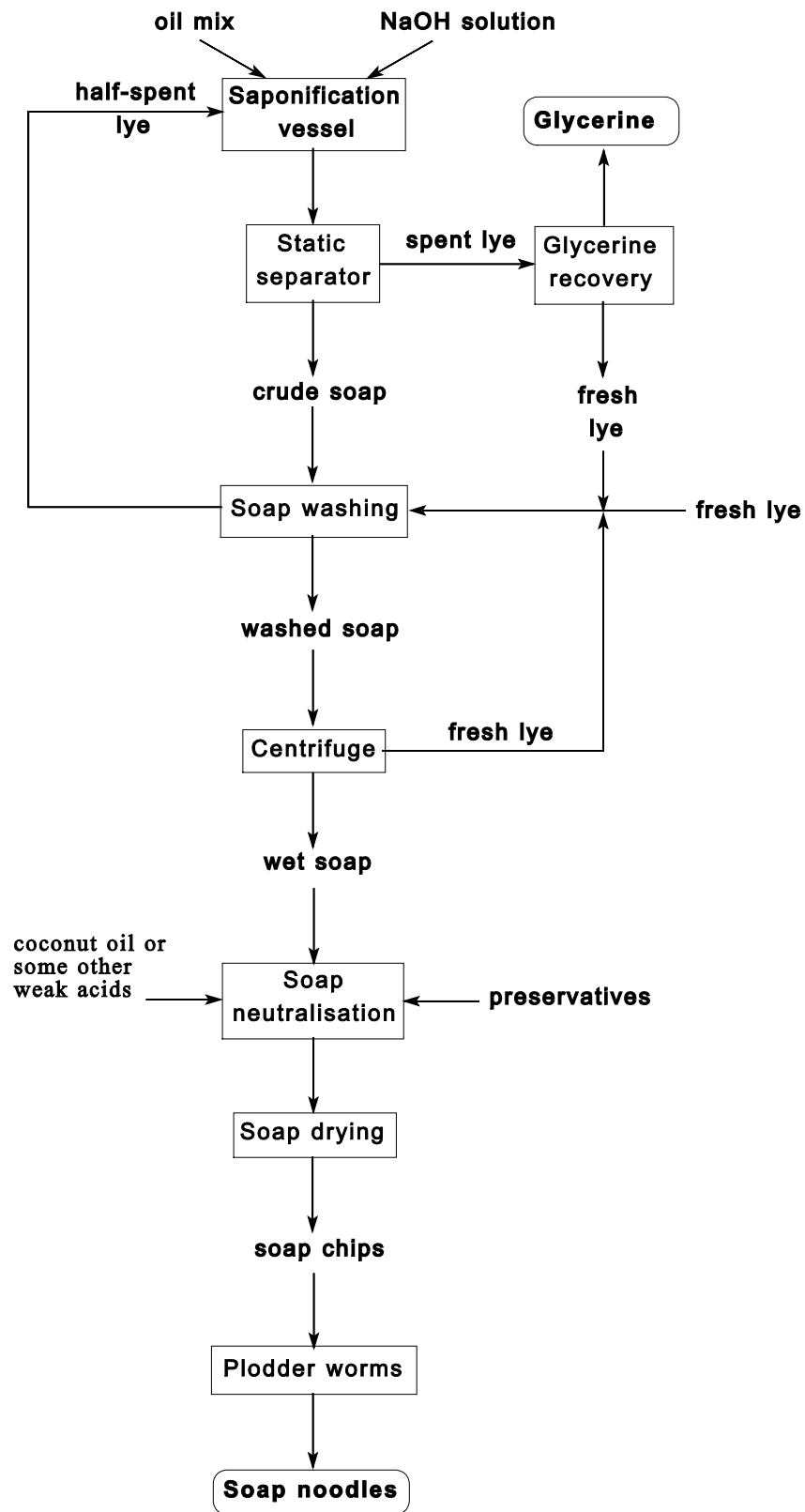


Figure 1 - The Colgate Palmolive continuous soap manufacturing process

These ingredients alone would give a low water, high glycerine soap. Soap needs to be about 30% water to be easily pumpable, and even then needs to be held at around 70°C, so excess lye is added to hydrate the soap and dissolve out some of the glycerine. The lye added is known as "half spent lye" and is the lye discharged from the washing column (see below). This lye already contains some glycerine, but it is further enriched by that formed in the saponification reaction.

Step 2 - Lye separation

The wet soap is pumped to a "static separator" - a settling vessel which does not use any mechanical action. The soap / lye mix is pumped into the tank where it separates out on the basis of weight. The spent lye settles to the bottom from where it is piped off to the glycerine recovery unit, while the soap rises to the top and is piped away for further processing.

Step 3 - Soap washing

The soap still contains most of its glycerine at this stage, and this is removed with fresh lye in a washing column. The column has rings fixed on its inside surface. The soap solution is added near the bottom of the column and the lye near the top. As the lye flows down the column through the centre, a series of rotating disks keeps the soap / lye mixture agitated between the rings. This creates enough turbulence to ensure good mixing between the two solutions.

The rate of glycerine production is calculated and the rate at which fresh lye is added to the washing column then set such that the spent lye is 25 - 35 % glycerine. Glycerine is almost infinitely soluble in brine, but at greater than 35% glycerine the lye no longer efficiently removes glycerine from the soap.

The soap is allowed to overflow from the top of the column and the lye ("half spent lye") is pumped away from the bottom at a controlled rate and added to the reactor.

Step 4 - Lye separation

The lye is added at the top of the washing column, and the soap removed from the column as overflow. As the lye is added near the overflow pipe the washed soap is about 20% fresh lye, giving the soap unacceptably high water and caustic levels. Separating off the lye lowers the electrolyte levels to acceptable limits.

The soap and lye are separated in a centrifuge, leaving a soap which is 0.5% NaCl and 0.3% NaOH, and about 31% water. The lye removed is used as fresh lye.

Step 5 - Neutralisation

Although the caustic levels are quite low, they are still unacceptably high for toilet and laundry soap. The NaOH is removed by reaction with a weak acid such as coconut oil (which contains significant levels of free fatty acids), coconut oil fatty acids, citric acid or phosphoric acid, with the choice of acid being made largely on economic grounds.

Some preservative is also added at this stage.

Step 6 - Drying

Finally, the water levels must be reduced down to about 12%. This is done by heating the soap to about 125°C under pressure (to prevent the water from boiling off while the soap is still in the pipes) and then spraying it into an evacuated chamber at 40 mm Hg (5.3 kPa). The

latent heat of evaporation lost as the water boils off reduces the soap temperature down to 45°C, at which temperature it solidifies onto the chamber walls.

The soap chips are scraped off the walls and "plodded" (i.e. squeezed together) by screws known as "plodder worms" to form soap noodles. The soap is now known as base or neat soap chip, and can be converted into a variety of different soaps in the finishing stages.

The moisture evaporated off the wet soap is transported to a barometric condenser, which recondenses the vapour without the system losing vacuum. The moisture can contain soap dust ("Fines") which is removed by cyclones and returned by augers to the spray chamber, while the water is recycled.

Base soap can also be made by a batch process such as that used by Lever Rexona.

The Lever Rexona Process

This process is summarised in **Figure 2**.

Step 1 - Oil preparation

The oils used most commonly are, as in the Colgate-Palmolive process, tallow and coconut oil. These are blended together and dried in a vacuum chamber. Once the oils are dry, bleaching earth is sucked by the vacuum into the chamber to remove any coloured impurities. The spent earth is landfilled and the oils stored ready for saponification.

Step 2 - Saponification

The mixture of bleached oils is mixed with spent lye from the washing stage (see below) and a caustic soda solution. The mix is heated and then left to settle into two layers. The neutral lye (which is now rich in glycerine) is pumped off and the mixture of soap and unreacted oils which has risen to the top is left in the pan. More caustic liquor is added to this and the mix reheated to saponify the remaining free oils.

Step 3 - Washing

The crude soap is then pumped to a divided pan unit (DPU) where it is washed by a counter-current of lye. This lye is a mixture of fresh brine solution and nigre lye (see below). The washed soap comes out the far end of the DPU and is sent to the fitting pans, while the lye comes out the near end and is pumped back into one of the saponification pans.

Step 4 - Fitting

Here the remaining unwanted glycerine is removed from the soap by reboiling with water, NaCl and a small amount of NaOH solution. The electrolyte concentration in the water is such that the soap and water separate out into two layers. The top layer is 'neat' wet soap, which is pumped off to be dried. The bottom layer is known as the 'nigre' layer, and consists of a solution of soap, glycerine and NaCl. This is left in the pan, reboiled with further salt and left to stand, forming a soap crust over a lower layer of nigre lye (salt and glycerine). This soap is left in the pan and is mixed with the next intake of washed soap, while the nigre lye is pumped back to the DPUs to wash the next batch of crude soap.

Step 5 - Drying

Moisture is flashed off under vacuum in the same manner as was described above for the Colgate-Palmolive process.

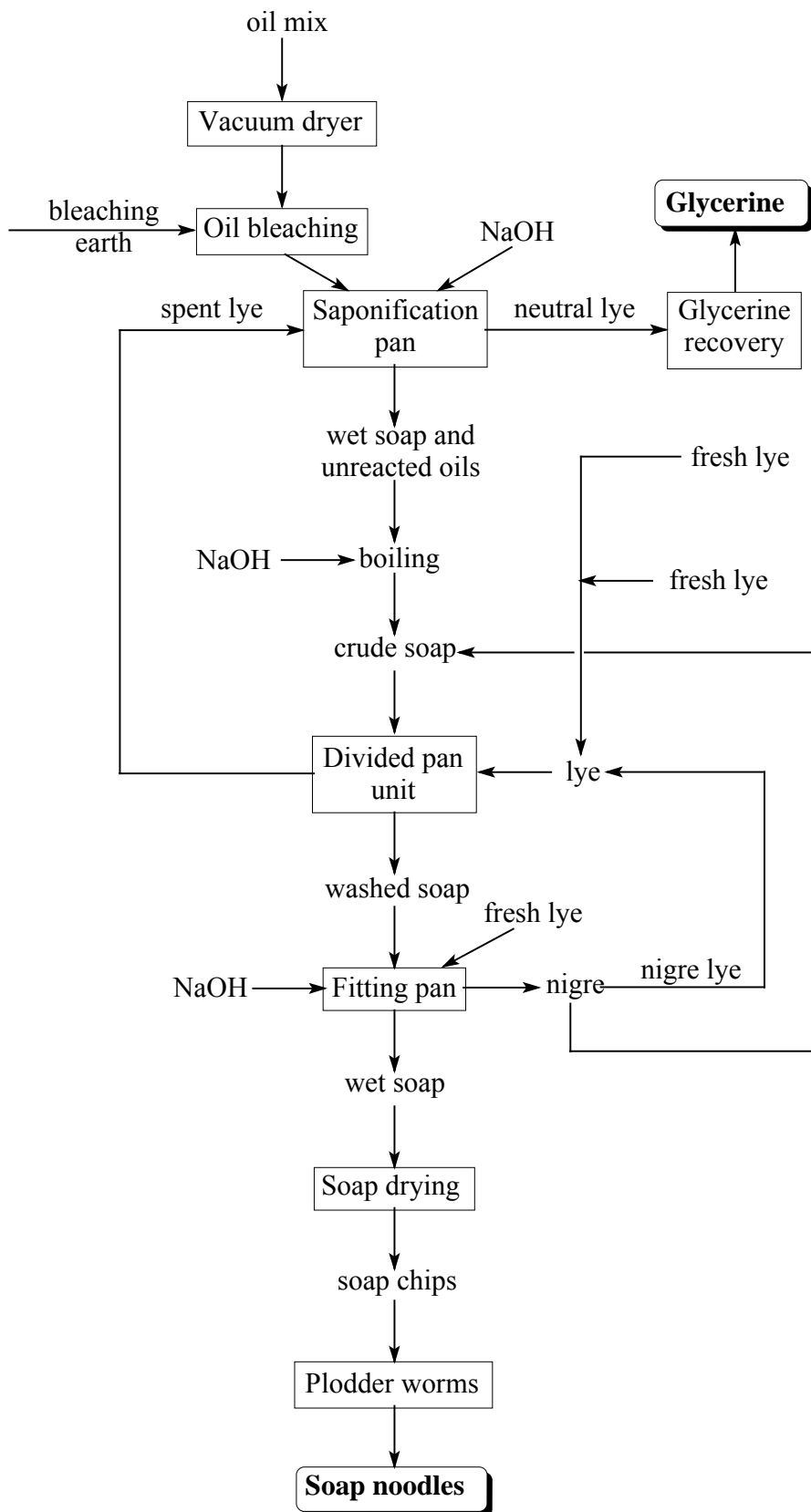


Figure 2 - The Lever Rexona soap manufacturing batch process

Laundry or 'hard' soap manufacture

The base soap is mixed with colour and preservatives and milled. Perfume is then added and the mixture plodded then extruded into a continuous bar. This, in turn, is cut into billets and stamped out into tablets ready for packaging.

Toilet soap manufacture

Toilet soap has less water and more fatty material (fatty acids and soap) than laundry soap. For this reason base soap intended for toilet soap manufacture usually has extra fatty acids added with the preservatives before it is vacuum dried. These ensure that there is no unreacted caustic left in the soap by the time it reaches the consumer, and also make the soap softer. Perfume, dye and opacifier are then added to the dried soap and the mixture milled to ensure even mixing. It is then plodded and extruded out as a continuous bar, cut into billets and stamped ready for packaging and sale.

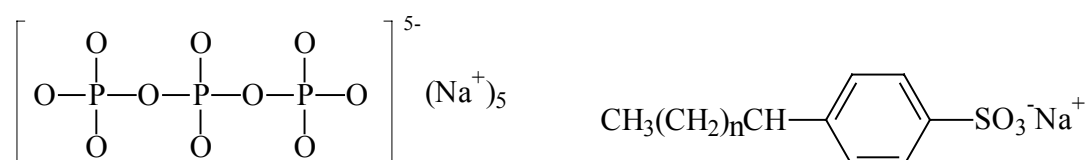
THE DETERGENT MANUFACTURING PROCESS

Detergents use a synthetic surfactant in place of the metal fatty acid salts used in soaps. They are made both in powder and liquid form, and sold as laundry powders, hard surface cleansers, dish washing liquids, fabric conditioners etc. Most detergents have soap in their mixture of ingredients, but it usually functions more as a foam depressant than as a surfactant.

Detergent powder manufacture

Step 1 - Slurry making

The solid and liquid raw ingredients (**Table 2**) are dropped into a large tank known as a slurry mixer. As the ingredients are added the mixture heats up as a result of two exothermic reactions: the hydration of sodium tripolyphosphate and the reaction between caustic soda and linear alkylbenzenesulphonic acid. The mixture is then further heated to 85°C and stirred until it forms a homogeneous slurry.



Step 2 - Spray drying

The slurry is deaerated in a vacuum chamber and then separated by an atomiser into finely divided droplets. These are sprayed into a column of air at 425°C, where they dry instantaneously. The resultant powder is known as 'base powder', and its exact treatment from this point on depends on the product being made.

Step 3 - Post dosing

Other ingredients are now added, and the air blown through the mixture in a fluidiser to mix them into a homogeneous powder. Typical ingredients are listed in **Table 3**.

Table 2 - The ingredients of detergent base powder

Solids	
Ingredient	Function
Sodium tripolyphosphate (STP)	Water softener, pH buffer (to reduce alkalinity).
Sodium sulphate	Bulking and free-flowing agent.
Soap noodles	Causes rapid foam collapse during rinsing.
Zeolite	Water softener (absorbs Ca^{2+} and Mg^{2+}) in countries where STP is not used; granulating agent for concentrated detergents.
Sodium carboxymethyl cellulose	Increases the negative charge on cellulosic fibres such as cotton and rayon, causing them to repel dirt particles (which are positively charged).
Liquids	
Ingredient	Function
Linear alkylbenzene sulphonic acid (LAS)	Surfactant - the main active ingredient
Caustic soda solution	Neutralises the LAS.
Coconut diethanolamide or a fatty alcohol ethoxylate	Nonionic detergent and foam former.
Fluorescer	Absorbs UV light and emits blue light, causing ageing cotton to appear white rather than yellow.
Water	Dissolves the various ingredients, causing them to mix better.

Liquid detergent manufacture*Step 1 - Soap premix manufacture*

Liquid detergent contains soap as well as synthetic surfactants. This is usually made first as a premix, then other ingredients are blended into it. This step simply consists of neutralising fatty acids (rather than fats themselves) with either caustic soda (NaOH) or potassium hydroxide.

Step 2 - Ingredient mixing

All ingredients except enzymes are added and mixed at high temperature. The ingredients used in liquid detergent manufacture are typically sodium tripolyphosphate, caustic soda, sulphonic acid, perfume and water. The functions of these ingredients has been covered above.

Step 3 - Enzyme addition

The mixture is cooled and milled, and the enzymes added in powder form.

Table 3 - Typical post dosing ingredients

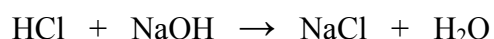
Ingredient	Function
Soda ash (anhydrous Na ₂ CO ₃)	Keeps the pH at 9.0-9.5. This ensures optimum detergent function. Also forms insoluble carbonates with Ca and Mg, so acts as a water softener.
Bleach (usually sodium perborate — NaBO ₃)	Bleaches stains without damaging colour-fast dyes. Sodium perborate breaks down at high temperatures to release H ₂ O ₂ , which functions this way.
Bleach activator (e.g. tetraacetythylenediamine)	Catalyses sodium perborate breakdown at low temperatures.
Enzymes (e.g. alkaline protease)	Alkaline protease breaks down proteins in the alkaline conditions created by soda ash, helping to remove stains.
Colour and perfume	Create a more asthetically pleasing product.

ANCILLIARY PROCESSES**Glycerine recovery**

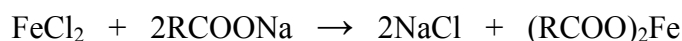
As has already been stated, glycerine is more valuable than the soap itself, and so as much of it as possible is extracted from the soap. This is done in a three step process.

Step 1 - Soap removal

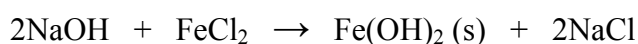
The spent lye contains a small quantity of dissolved soap which must be removed before the evaporation process. This is done by treating the spent lye with ferrous chloride. However, if any hydroxide ions remain the ferrous ions react with them instead, so these are first removed with hydrochloric acid:



The ferrous chloride is then added. This reacts with the soap to form an insoluble ferrous soap:



This precipitate is filtered out and then any excess ferrous chloride removed with caustic:



This is filtered out, leaving a soap-free lye solution.

Step 2 - Salt removal

Water is removed from the lye in a vacuum evaporator, causing the salt to crystallise out as the solution becomes supersaturated. This is removed in a centrifuge, dissolved in hot water and stored for use as fresh lye. When the glycerine content of the solution reaches 80 - 85% it is pumped to the crude settling tank where more salt separates out.

Step 3 - Glycerine purification

A small amount of caustic soda is added to the crude glycerine and the solution then distilled under vacuum in a heated still. Two fractions are taken off - one of pure glycerine and one of glycerine and water. The glycerine thus extracted is bleached with carbon black then transferred to drums for sale, while the water/glycerine fraction is mixed with the incoming spent lye and repeats the treatment cycle.

ENVIRONMENTAL IMPLICATIONS

Soap is designed as a product to be used once then flushed down the drain, so as expected the environmental implications of its manufacture are not nearly so great as many other chemical processes. There are two main areas of concern: the safe transport and containment of the raw materials, and the minimisation of losses during manufacture.

The three main components of soap by both cost and volume are oils, caustic and perfumes. Oils and perfume are immiscible in water and if spilled create havoc, although the oils do solidify at room temperature. Transport of these products is by trained carriers, and the systems for pumping from the truck to storage tanks is carefully designed. Perfumes are bought in lined steel drums which are quite robust, and flammable perfumes are not used in soaps.

All storage tanks are surrounded by bunds to catch the contents of a tank should it rupture or a valve fail. When the storage system is designed, all the safety features (such as access to tank and valves) are designed in, as well as procedures to deal with the product should it end up in the bunded area.

Within the plant, all the process areas are also bunded, and the trade waste from there piped to an interception tank before draining to the council's trade waste system. The contents of the interception tank are continuously monitored for acidity or alkalinity, and is designed to settle out excess solids or light phase chemicals. If a spill is detected in the plant itself, a portion of the interception tank can be isolated off and the effects of the spill neutralised before the waste is dumped.

In most cases, however, potential problems are identified and stopped before they happen. Often an off-spec product can be reprocessed and blended rather than dumped, and even washout water can be reprocessed to minimise the discharges from the plant.

Finally, the manufacturing process itself is closely monitored to ensure any losses are kept to a minimum. Continuous measurements of key properties such as electrolyte levels and moisture both ensure that the final product is being made to spec, and ensures the manufacturing process is working as it was designed to. Hence the losses in the plant will indirectly be minimised because the process itself is being monitored.

Synthetic detergent biodegradability

There has recently been a strong move away from the environmentally hazardous biologically stable detergents used in the past to biodegradable ones. The sulphonic acid and nonionic detergents used in New Zealand to produce both liquid and powder detergents are fully biodegradable and comply with the relevant Australian standard. The sulphonic acid is made from a highly linear alkylbenzene, mainly dodecylbenzene, and the nonionics are ethoxylated long chain alcohols. The sodium lauryl ether sulphates also used in liquid

detergents and shampoos are highly biodegradable, being made from either natural or synthetic linear C₁₂ - C₁₅ alcohols. Phosphates from detergent products used in New Zealand are independently monitored and have been found to not be an environmental hazard.

Detergent powder

Detergent powder manufacture has some specific environmental issues associated with it that are not present in other areas of the industry. These are dust control and volatile organic emissions. Dust present during delivery and transfer of bulk powdered detergent (and powdered raw materials) is a potential problem. Dry and wet cyclones are used to filter out most of the dust, and all emissions are monitored. If the dust level in these does exceed acceptable limits, appropriate remedial action is taken. Dust levels in emissions must be kept below 50 mg m⁻³.

The spray drying tower also releases volatile organics. These emissions are minimised by having tight specifications on what can be added as primary detergent active material. Any potentially hazardous material is added with the secondary actives after the tower so that it is not heated. Spot checks are done on the total hydrocarbon content of the exhaust gases using a flame ionisation detector.

ROLE OF THE LABORATORY

The laboratory monitors the formulation and specification of products from raw material to finished goods. Many soaps are formulated locally, and the laboratory tests a range of formulations for stability and manufacturing practicality. The trial formulations are aged in a warm oven to simulate a couple of years of shelf life, then checked for perfume loss or alteration, base odour, colour stability and any general rancidity. Formulations are also constantly checked for cost effectiveness, and soaps are frequently reformulated for cost and supplier considerations.

When a new formula has been agreed the laboratory will lay down the specifications that the finished soap and its intermediary stages must meet. These could be colour, odour, moisture or electrolyte concentrations, or the concentrations of impurities or additives. These specifications are also constantly being revised as the production equipment is improved, or consumer demands change.

The laboratory lays down all the specifications for raw materials to be purchased against. These specifications become the basis for the supplier to quote against. The materials are constantly tested against these specifications, either on a shipment basis or supplier's batch size. In some cases the manufacturing plant is inspected and approved, and if the supplier can validate their process then the need for many routine or expensive tests can be reduced or eliminated.

In most cases quality testing is performed at the process, by the process operators. The laboratory hold samples of every batch of finished goods for twelve months, so that if there are any consumer complaints, an original sample can be tested against the defect sample to determine the cause of the complaint.

Tests carried out on some particular products are listed below.

Batch process soap

The incoming tallow and coconut oil are tested for colour (after bleaching) and free fatty acid content. The neat liquid soap is tested for free alkali, salt content and glycerol content, while the soap chips are tested to moisture and fatty acid content.

Detergent powder

On-line tests are continuously carried out on density and moisture. The laboratory also tests for the concentrations of active detergent, sodium tripolyphosphate, moisture, soda ash, enzymes and bleach, and monitors physical properties such as dynamic flow rate, compressibility, particle size, colour and perfume.

Liquid detergent

The product is typically tested for viscosity, pH, cationic detergent (fabric conditioner) content, enzyme content, conductivity (a measure of detergent stability), colour and perfume.

Compiled by Heather Wansbrough from two articles, one from Ralph Laing (Colgate-Palmolive) and the other from Paul Milson (Lever Rexona) and with reference to:

- *The Encyclopædia Britannica (15th ed.)*; Encyclopædia Britannica, Inc.; 1979
- Selinger, Ben; *Chemistry in the Marketplace (3rd ed.)*; Harcourt Brace Jovanovich; 1986