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Soap, Detergents and Washing

In primitive societies, even today, clothes are cleaned by beating them on rocks near a stream. Certain plants, such as soapworts, have leaves that produce saponins, chemical compounds that give a soapy lather. These were probably the first detergents people used. True soap is solely made up of fats that when mixed with a strong alkali produce "salt" through a chemical reaction called saponification. The products of the reaction are two: soap and glycerine. Water is also present, but it does not enter into the chemical reaction. The water is only a vehicle for the alkali, which is otherwise a dry powder. The water is evaporated during the curing process, which depending on the fats used, can be anywhere from six weeks to six months.



"The earliest recorded evidence of the production of soap-like materials dates back to around 2800 BC in ancient Babylon." A formula for soap consisting of water, alkali, and cassia oil was written on a Babylonian clay tablet around 2200 BC. The Ebers papyrus (Egypt, 1550 BC) indicates the ancient Egyptians bathed regularly and combined animal and vegetable oils with alkaline salts to create a soap-like substance.

The name saponification literally means "soap making". The root word, "sapo", is Latin for soap. The Italian word for soap is sapone. The oils used in modern handmade soap are carefully chosen by the soap maker for the character they impart to the final soap. Coconut oil creates lots of glycerine, makes big bubbly lather, and is very stable. Olive oil has natural antioxidants and its soap makes a creamier lather. The proper recipe and cure can produce a very gentle bar.

If you look up detergent in a dictionary it is simply defined as cleaning agent. During the last three to four decades, however, the word detergent has tended to imply synthetic detergent, rather than the older soap. In fact, commercial formulations consist of a number of components, and we shall use the term surface-active agent, or its abbreviation surfactant, to describe the special active ingredients that give detergents their unusual properties.

Soap, by this definition, is a surfactant. In fact, it is the oldest one and has been in use for over 5000 years. Some soap manufacture took place in Venice and Savona in the fifteenth century and in Marseilles in the seventeenth century. By the eighteenth century, manufacture was widespread throughout Europe and North America, and by the nineteenth century the making of soap had become a major industry. As a matter of fact, soap became a detergent in 1907 when a German company put the product "Persil" on the market. In addition to the carboxylic acid soap, "Persil" contained sodium perborate, sodium silicate and sodium carbonate. Hence perborate + silicate = PERSIL".

You may well ask why soap, which served well for so many years, was eventually displaced. Soaps are cheap and they are manufactured from a renewable source, whereas many of the synthetic detergents are made from petrochemicals. Soaps are also biodegradable; that is, they are readily broken down by bacteria, and thus they do not pollute rivers. However, due to their gelling properties, soaps do have a greater tendency to clog sewerage reticulation systems than synthetic detergents. The grease trap of a non-sewered house, for example, was often laden with soap. But the most important reason for the displacement of soap is the fact that, when a carboxylic acid soap is used in hard water, precipitation occurs. The calcium and magnesium ions, which give hardness to the water, form insoluble salts with the fatty acid in soap and a curd-like precipitate occurs and settles, of course, on whatever is being washed. By using a large excess of soap, it is possible to re-disperse the precipitate, but it is extremely sticky and difficult to move. This problem with soap can be demonstrated by a simple

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experiment in which a concentrated solution of hard-water salts is added to a 0.1% solution of soap and also to a 0.1% solution of synthetic surfactant. The soap precipitates, but the synthetic surfactant remains clear because its salts are water soluble.

Water, Hard or Soft? You may live in an area where the water is extremely soft, but calcium and magnesium ions are present in the dirt that you wash out of your clothes, so that some precipitation still occurs if soap is used, and gradually deposits are built up in the fabric. There are other disadvantages with soap; it deteriorates on storage, and it lacks cleaning power when compared with the modern synthetic surfactants, which can be designed to perform specialised cleaning tasks. Finally and very importantly from a laundry point of view, soap does not rinse out readily; it tends to leave a residue behind in the fabric that is being washed. A residue gradually builds up and causes bad odour, deterioration of the fabric and other associated problems.



What's the difference between a surfactant and soap? In general terms, the difference can be likened to the difference between cotton and nylon. On the one hand, soap and cotton are produced from natural products by a relatively small modification. On the other hand, synthetic surfactants and nylon are produced entirely in a chemical factory. Synthetic surfactants are not very new, either. Back in 1834 the first forerunner of today's synthetic surfactants was produced in the form of a sulphated castor oil, which was used in the textile industry.

The development of the first detergents in an effort to overcome the reaction of soaps with hard water provides a good illustration of one of the standard chemical approaches. If a useful substance has some undesirable property, an attempt is made to prepare an analogue, a near chemical relation, which will prove more satisfactory. The petroleum industry had, as a waste product, the compound propylene, $\text{CH}_3\text{-CH=CH}_2$, which formerly was burnt off. By joining four of these propylene molecules together and if benzene is attached at the double bond, the resulting compound reacts with sulphuric acid. Then sodium hydroxide is added to neutralise the sulfonic acid (or sulphonic acid) and a sodium salt is obtained. The new substance is closely related to an ordinary soap, and is an excellent detergent. Sodium dodecylbenzenesulfonate, an alkylbenzenesulfonate surfactant used in laundry detergents.

The relationship between foaming power and detergency has always been of interest, and foaming power has become associated in many consumers' minds with high detergent power. The first liquid detergent on the domestic Australian market was "Trix". It was non-foaming, so was soon replaced because of consumer resistance. However, it is generally conceded by detergent technologists that foam height has no direct relationship to cleaning power in ordinary fabric washing systems. In systems where the amount of washing fluid is low, foam may play an important role. The individual foam films tend to take up and hold particles of soil that have been removed from the item, preventing them from being re-deposited and allowing them to be washed or scraped away. Front loading washing machines work by bashing clothes against the side of the cage - the high tech version of beating clothes on rocks. In domestic machines front loaders clean clothes better than top loaders, but only if a low-suds detergent is used, because the suds cushion the impact and reduce the cleaning action.

Synthetic detergents dissolve or tend to dissolve in water or other solvents. To enable them to do this, they require distinct chemical characteristics. Hydrophilic (water loving) groupings in their molecular structure, and hydrophobic (water hating) groupings, help the detergent in its "detergency" action.

This detergency depends on the balance of the molecular weight of the hydrophobic to the hydrophilic portion. This is called the HLB value, and can range from 1 upwards. HLB is Hydrophilic-Lypophilic Balance. As the HLB value increases, the product can tend towards being a paste or solid. The lower number HLB values tend to be less water soluble, and more oil soluble. The higher the HLB the more water soluble the product.

Mixtures of low and high HLB detergents produce good detergents to handle oil, fat and grease, the higher HLB detergent helps solubilise the less water soluble, low HLB detergent into an aqueous system.

Water is an important basic commodity in a laundry and in general its availability is reducing and its price is increasing, and the subsequent effluent disposal is also a major factor to be considered with consequences on costs, as well as environmental. Drinking water that is considered safe does not necessarily mean it is suitable for washing unless it is further treated in some way and a good launderer will have checked carefully the suitability, as well as volume of supply.

The Impact of Professional Laundering on the Environment

A Laundry will unavoidably have an impact on the environment, not least because of all the chemicals used. However, it must be said that the effluent resulting from a laundry is certainly no worse than that resulting from domestic washing, albeit on a larger scale at the local level. A laundry is generally much more efficient in its use of detergents

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Clean up

etc. However, a launderer should be aware of the chemicals he/she is using and of their potential for environmental damage.



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Replacement of Phosphates

One important effect to which the use of detergents contributes is the eutrophication of water courses. Eutrophication is the disruption of the natural balance and productivity of a water course caused by excessive algal growth. Phosphates reaching the water course from various sources assist this process because phosphates are essential nutrients for the growth of algae and are generally the limiting factor to that growth. Phosphates were once used in detergents and they performed several essential cleaning functions particularly well: They helped to soften the water. They helped to break up the dirt on the fabrics and prevent the dirt from being redeposited, thereby ensuring a hygienic, and recyclable textile product. Phosphates were ideal in many ways since they are non-toxic and they do not corrode metals in the washing machine. Phosphate-free products are now available although the influence of their use on the overall phosphate levels is debatable. Laundry and domestic detergents were considered to account for approximately 20% of the phosphate levels found in effluents. By far the greater proportion of this arises from domestic washing. Although increased sewage treatment can help control a problem of excessive phosphate by 'phosphate stripping' this is an expensive procedure and also it is difficult to achieve complete removal.

Biodegradability

Biodegradable is a term applied to any organic material that breaks down to simpler units by the natural action of living organisms. Generally, the synthetic soaps (surfactants) used in detergent formulations must be greater than 95% biodegradable during their residence time at the sewage treatment works. Ironically, it is this ability to break-down in the environment which results in the COD (Chemical Oxygen Demand) charges on the water bills of the larger laundry. However, the most visible effect of biodegradability is the absence of foam in water ways which in the 1960's used to be an all too common sight.

Bleaches

Bleaches are used in the removal of coloured staining and the disinfection of surfaces or fabrics. Both of these processes are achieved by a process called oxidation, which unfortunately also attacks textiles reducing their useful life.

There are two types of bleach in laundry use:

Oxygen based bleaches eg, hydrogen peroxide. This type of bleach requires heat and time to achieve effective stain removal and is a comparatively poor disinfectant. However, it breaks down into harmless substances (water and oxygen) and therefore does not damage the environment directly.

Chlorine based bleaches eg, sodium hypochlorite. This type of bleach reacts quite rapidly and although it is regarded as being biodegradable, under certain acidic conditions it can liberate chlorine which is very toxic. One of its decomposition products is salt which can be corrosive.

Enzymes

Enzymes are based on natural substances which assist in the breakdown (digestion) of organic matter. Since about the middle of the last century enzymes have been used in some washing products to help remove stubborn protein soil, such as egg and blood. Concern has been expressed in the past that enzymes could possibly lead to skin complaints. However, better control of the working environment and encapsulation of the enzymes in the products has reduced the risk. The enzymes used in industrial detergents are designed to work in the condition of the first low temperature wash and are destroyed in the subsequent high temperature wash.

Benefits It must be stressed, however, that there are many benefits to the environment as a result of the commercial laundering of textiles. Washing in the domestic situation is important to maintain personal hygiene standards and to prevent the spread of germs around the home. However, a commercial laundry offers many advantages over domestic washing. The washing procedures used in a laundry are optimised, maintaining much higher standards. This may be important for the cleaning of workwear which may be prone to heavy soiling, or bacterial contamination. It is particularly vital in a hospital laundry where heavily stained and contaminated work is processed. Specific temperatures and bleach concentrations are vital in this situation to ensure the complete destruction of any bacteria which may be present. The rigorous washing standards that exist in a laundry could never be matched in a domestic washing machine, and Hotels benefit from the consistent high standards produced and has long seen the advantages.

A commercial wash is much more efficient in its use of resources than a domestic washing machine. Industrial laundry machines use much less water and thus require fewer supplies to maintain the same concentrations in the wash liquor. In addition, recycling both water and heat makes an industrial laundry 300% - 400 % more efficient than domestic washing. Also, domestic washing machines usually use electricity to heat the water, whereas a commercial laundry uses other means which are far more energy efficient.

Another major benefit of professional laundering is that it enables textiles to have an extended life, and sometimes to be recycled for further use and wear. The alternative to laundering would be to dispose of all soiled articles and

replace with new. In addition to the practical problem of disposing of large quantities of soiled non reusable garments and linen, there are the additional costs of manufacturing new textile articles in terms of energy and materials.

Laundries therefore have a net positive effect on the environment, and on a country's economy, and there are many ways in which the negative effects of a laundry can be minimised further eg, through good housekeeping, maintaining good working practices and by the efficient use of all resources.

SOILING AND ITS PROBLEMS IN WASHING In a cleaning and washing context, soil or dirt is classically defined as matter in the wrong place. Here we examine the origins, nature and tenacity of a typical laundry washing soils, the factors which affect their removal, and gives an introduction to the basic methods used in the cleaning or washing process.

Soils themselves arise from the most everyday activities:

SOIL TYPES Soils vary enormously in composition, properties and degree and are often complex heterogeneous mixtures. They can, however, be broadly divided into five categories: oily, particulate, proteinaceous, stains and miscellaneous.

Oily soils range from the dirty motor oils of the engineering industry to the fats and oils of animal/vegetable origin and body fat (sebum). These organic soils are often associated with proteins and staining materials in food soiling and with carbon and metal particles in mineral oils and greases.



Particulate soils are made up of such things as clay, carbonaceous matter, dust, pigments and metal oxides. They originate from the atmosphere or from a manufacturing/industrial process and are often fairly simple inorganic materials of very small dimensions. These soils rarely exist on their own on laundry textiles, usually they are found embedded in oily/greasy matter.

Proteinaceous soils are those special protein-based solids that originate from meat and fish industries and also the skin flakes of garment wearers (dead skin from normal body regeneration processes). Invariably they are associated with fatty and/or coloured matter. Stains are the coloured residues of soils left after normal washing. In general they can be divided into non-removable, apart from special treatments such as rust, ink and paint and other kinds such as protein-based stains from grease, blood, body greases, fruit and tea, coffee, wine and beer colourings.

Miscellaneous soils, already described by basic type, merit a special mention due to their origins. They embrace carbohydrates from food, residual soaps and hardness salts on towels, bleeding dyes from coloured work, soils amended and redistributed/re-deposited during washing ("wet-soiling") and residual soil from inadequate washing over a period.

SOIL ADHERENCE TO FABRICS Soil adherence is directly related to the chemical nature and physical characteristics of both fabric and soil. The major factors involved are:

Fibre type, yarn structure and weave of the fabric; Liquid or solid state of soil and its particle size; Presence of oily matter; Presence of water; Conditions at time of soiling, e.g. temperature, humidity, rubbing.

The forces and mechanisms which operate to make soil hold on to fabrics are of mechanical, chemical and electrical origin. The simplest soil can be lodged in the spaces between the yarns in the weave: liquids and small particles may even be able to occupy areas between fibres and in the irregularities on their surfaces.

More positive binding effects, however, are due to the mutual wetting of like materials - oily soils to polyester and water-based to cotton: electrostatic attraction - negatively charged fabric attracting positively charged soils: the bridging effect of polyvalent cations such as water hardness metals - effectively changing the charge on fibre surfaces thus attracting negatively charged soils: hydrogen bonding and Van Der Waal's forces (inter-molecular attraction). In extreme cases, soils may even become an integral part of a fibre surface by chemical linkage.

Such soil is simply "attached" to fabrics by being part of an oily mixture and owes its adhesion to the absorption of oil into the fabric. The binding and spreading (wicking) of oily soils and its contaminants is clearly seen on work wear, especially at collars, cuffs, elbows, knees and midribs.

Molecular and particle size can influence adhesion dramatically. Large molecules, such as denatured (heated) protein, provide cohesive forces - which hold the soil itself tightly together, and many bonding sites - which hold the soil to the fabric. Small particles can exhibit enormous surface-bonding forces: below about 1-2 microns they are virtually irremovable.

SOIL REMOVAL The major factors affecting this process are:

Nature of the soil(s) and fibre(s)/fabrics; Nature of the soil/fibre bonds; Water hardness; Mechanical action; Detergent concentration and effectiveness; Duration and temperature of the process.

In addition to the vital contributions of mechanical action (washing machine) and water, many physical and chemical reactions are needed to achieve soil removal. This is brought about in two ways:-

1. By breaking the bonds holding soil and fibre together -

a). by physical action - using surfactants to lower the inter-facial tension between soil and fabric, soil and water and fabric and water;

- (b) by chemical action - using -chelating agents to prevent hard water ions interfering or forming scale.
2. By breaking the soil down –
- (a) with surfactants to dissolve and disrupt the adhesive film of oils and grease;
 - (b) with alkalis to saponify and hydrolyse fatty soils, hydrolyse proteins and peptise particulate matter;
 - (c) with bleaches to solubilise and decolourise stains and other residues;
 - (d) with enzymes to solubilise proteins.

SOIL SUSPENSION Soil removed during a wash process needs to be held in suspension or in a stable solution form until the process is finished. Inadequately stabilized systems allow soil to redeposit, producing an overall greying of whites and dulling of coloureds. Small particles and liquefied oil matter are most likely to be re-deposited. On cottons it is usually particulate matter that redeposit. On synthetics it is usually fatty soil. Greying due to these causes must be avoided as it is very difficult to remove; such soil is much finer and held more strongly than ever on the fabric and may even penetrate deeply into the fibres. In the worst cases it is impossible to remove it totally and regain the original whiteness or colour of the fabric.

Mechanisms which increase the soil holding capacity of detergent liquor and overcome the ill effects of draining the soil-laden liquor through cleaned fabrics and carrying some over into the rinses, include the following:

Stabilising soil suspension in the wash liquor by –

- (a) using alkali, anionic surfactants and hydrophilic polyelectrolyte's (e.g. CMC) to increase the negative charges on soil particles and fabric surfaces;
- (b) introducing non-ionic surfactants and anti-redeposition agents to solubilise oil soil, prevent particle collision and decrease adverse electrical interactions between soil/soil and soil/fabric;
- (c) using chelating agents to neutralise positively charged water hardness metals to prevent soil coagulation.

2. Improving the resistance of synthetic and resinated fabrics to oily redeposition by applying hydrophilic soil release finishes. Examples of fabrics treated in this way are Klopman's Miraclean and Tootal's SRF Polycotton twills.

SPECIAL PROBLEMS Most soils become much more tenacious if allowed to "dry-in" or "age". This is true of water-borne clay and carbonaceous particles as well as fatty materials which oxidise and polymerize to form detergent-resistant residues. Inadequate washing followed by finishing is an essential rapid 'ageing' mechanism. Workwear, especially in mining, heavy engineering and power generation industries, becomes very heavily soiled with oil-based soiling. Many of these garments are made from polyester cellulosic fabrics which absorb little water but readily soak up oil. This makes them easy to "finish" but difficult to clean. Special wash processes are needed which use high levels of detergent especially specific non-ionic surfactants. Fabrics treated with special hydrophilic finishes are helpful in these situations. In food industries processing meat and fish (abattoirs, broiler chicken factories, etc.) garments are often soiled with gross amounts of fatty proteinaceous matter and blood residues. Ageing and prematurely high temperature washing processes denature such soils and make them extremely tenacious. Chemical treatments (e.g. caustic, bleach or enzymes) are usually needed. Treatments designed to improve oil-shedding properties of fabrics tend to exacerbate the protein and water-borne soil problems.



SUMMARISED Soils and stains vary greatly in nature, intensity and age, and the complex ways in which they adhere to different fabrics provides varying degrees of difficulty in removal and suspension. Water, mechanical energy and heat need the specific physio-chemical contributions of detergents to overcome the forces bonding soils to fabrics.