# Detergents – Zeolites and Enzymes Excel Cleaning Power

*B S Sekhon and Manjeet K Sangha*

**Presently used detergent formulations generally consist of surfactants, builder and cobuilder, bleaching agents, additives for secondary benefits and enzymes. Zeolites are basically hydrated crystalline aluminium silicates which function as ion exchangers and make the water soft by removing calcium, magnesium and other ions. The different zeolite types A, P, X and AX and their advantages over previously used phosphate builders are described. The emphasis on compact detergents has increased the demand for zeolite builders. Enzymes in detergent formulations are stable at high pH and temperature and remove the stubborn stains of proteins and lipids by converting the larger stains into smaller water soluble fragments. Enzymatic detergent requires low workable temperature, low mechanical energy and is less toxic and non-corrosive.**

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People in the past used to clean their clothes by beating wet textiles on rocks near a stream. In this process water dissolved the stains generally composed of sugars, salts and dyes. However, oily soil was difficult to remove this way and remained attached to the fabric. The oldest substance used for removal of oily stains is soap, the sodium salt of a long chain fatty acid, for example, sodium stearate (I)

$$CH_3\,(CH_2)_{16}\text{ - }COO^-\,Na^+ \qquad \text{(I)}$$

| Hydrophobic part | Hydrophilic part |
|---|---|

The wash performance of soap decreases in hard water, due to the formation of insoluble calcium and magnesium salts of the fatty acids by replacing the sodium ions. The precipitated soap becomes useless for stain removal.

Keywords
Zeolites, surfactants, enzymes.

## Detergents

A detergent is a mixture of substances primarily used for laundry and dish washing. The core components of most modern detergents are surfactants, builder and cobuilder, bleach and bleach activator, and special additives such as fluorescent brightener, filler, corrosive inhibitor, antifoaming agent and enzymes. A detergent may contain more than one type of surfactant.

## Surfactants

These are surface-active agents with wetting, detergent and emulsifying properties. A simple classification of surfactants is based on the nature of the hydrophobic group. Four classes of surfactants are given in *Table* 1.

A useful index for choosing surfactants for various applications is the hydrophilic-lipophilic balance (relative percentage of hy-

***Table 1. Classes of surfactants.***

| Type | Composition | Example | Structure |
|---|---|---|---|
| Anionic | Sulfonated alcohols ($C_{12}$-$C_{18}$). Detergency is vested in anion part. | Sodium lauryl sulfate<br>Sodium alkyl benzene sulfonate. | $C_{12}H_{25}OSO_2\ O^-Na^+$<br>$R\ CH\ (CH_3)\ C_6H_4\ SO_3^-\ Na^+$ |
| Cationic | Quaternary ammonium salts. Detergency is due to cation. | Hexadecyltrimethyl ammonium bromide. Generally used as germicides and fabric softners. | $C_{16}\ H_{33}\ N^+\ (CH_3)_3\ Br^-$ |
| Non-ionic | Condensation product of long chain alcohol and 7-8 ethylene oxide units. | n-dodecyloctaethylene glycomonoether ethoxylate. | $H_3C(CH_2)_{10}\ CH_2(OCH_2CH_2)_8$ OH<br>H-bonding to many 'O' atoms makes the polyether end of the molecule water soluble. |
| Zwitterionic/ Amphoteric | Contain both acidic and basic groups. Most common amphoterics are N-alkyl betaines. | Laurylamido propyl dimethyl betaine (used in shampoos, skin cleaners). | $C_{12}H_{25}CON^+(CH_3)_2CH_2COOH$ |

drophilic to lipophilic groups in the surfactant molecules) and its range for application of surfactants as detergents is 13-16. All surfactant molecules have a water soluble (hydrophilic) and a water resistant (hydrophobic) part. At critical micelle concentration ($10^{-4} - 10^{-2}$ M), individual surfactant molecules spontaneously aggregate into micelles. The hydrophobic ends of surfactant molecules attach to oil and grease particles to form swollen micelles, which dissolve in water by the attraction of the hydrophilic ends to the surrounding water. The cleaning power of detergents is provided by their surface-active properties.

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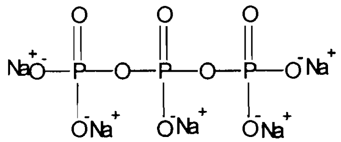
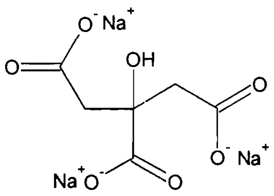
## Builders

The builder in detergent is the second major component, which at lower concentration enhances the effect of the surfactant by deactivating calcium, and magnesium ions, which would otherwise use up surfactant molecules. Builders are thus water softeners and work by complexation (sodium tripolyphosphate STP), precipitation (sodium carbonate) or ion-exchange (zeolites). Both organic (STP and sodium citrate) and inorganic (natural and synthetic) materials were used as builders earlier.



STP



Sodium citrate

The most common builders used today are synthetic zeolites. Zeolites are solid ion exchangers which trap the divalent ions inside the solid particles and are used for the production of biodegradable detergents. The chronology of the development of detergent builders is given in *Table* 2.

Zeolites are hydrated crystalline aluminium silicates of natural or synthetic origin with pore size of molecular dimension (0.3-1nm) and have a three-dimensional framework composed of tetrahedral $AlO_4^{-5}$ and $SiO_4^{-4}$ units that are linked by oxygen

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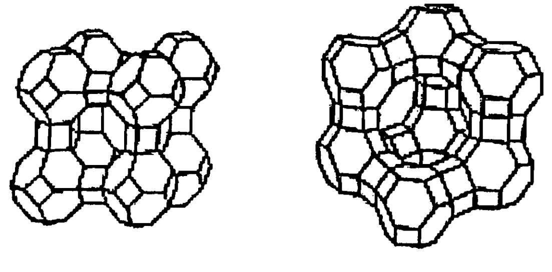
| Builder (all builders as sodium salts) | Year |
|---|---|
| Silicate + Carbonate | 1907 |
| Phosphate containing detergents | |
| Diphosphate | 1933 |
| Triphosphate | 1946 |
| Zeolite A + triphosphate | 1976 |
| Phosphate free detergents | |
| Zeolite A + Carbonate + Polycarboxylates | 1983 |
| Zeolite A + Amorphous or Crystalline disilicates + polycarboxylates | 1994 |
| Zeolite P + Carbonate + Citrate or Polycarboxylate | 1994 |
| ZeoliteX + Carbonate + Citrate or Polycarboxylate | 1997 |
| Zeolite AX (Zeolite X (80%) + Zeolite A (20%) | Recent development |

***Table 2. Chronological development of detergent builders.***

atoms. The tetrahedral atoms (Al and Si) are connected by bent 'O' bridge. One such structure called sodalite cage or $\beta$cage consists of eight-6-sided or 6-oxygen rings or six rings and six 4-rings. An important class of zeolites is based on sodalite cage. The more common zeolites available for detergents of commercial importance are type A, P, X and AX, and all have significantly different structures, Si/Al ratio, and pore size. Connecting $\beta$cages on their 4-ring sides by cubes or double 4-rings gives zeolite A (Si/Al = 1) of the formula $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].xH_2O$. A larger cage called $\alpha$-cage is formed in the middle of the structure having 0.41 nm free excess diameter which allows calcium ions to diffuse more easily than magnesium ions. Zeolite P has higher calcium exchange capacity than zeolite A as its pore diameter of 0.3 nm allows calcium ions to be bound more firmly than in zeolite A.

Connecting sodalite cages on their 6-ring sides by hexagonal prisms or double 6-rings gives a structure called faujasite, which is zeolite X of composition $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}].xH_2O$. Zeolite X exchanges magnesium ions more readily due to larger pore diameter (0.74 nm) as compared to zeolite A and zeolite P. Zeolite AX (a co-crystallite composed of 80 per cent zeolite X and 20 per cent zeolite




A) shows calcium and magnesium exchange properties better than those of a blend of the pure zeolites. Zeolites P, X and AX are superior to zeolite A due to their rapid ion exchange capability at low washing temperatures.

During the last decade, the trend towards compact detergents increased the demand for zeolite builder. Zeolite A is now a builder leading to compact and super compact detergents. The compact detergents emerged in 1992 and super compact detergents in 1998 which are characterized not only by particularly low dosage and thus high surfactant content, but also by an increase in bulk density (regular powder, 500-600 g/l, supercompact, 800-900 g/l and tablets, 1000-1300 g/l). Tablets represent the latest development in laundry detergents, which also require highly absorptive zeolite builders.

A typical composition of powdered traditional and compact detergent formulation is given in *Table* 3.

*Advantages of Zeolites over other Builders*

i) They offer very high product stability and no decomposition; (ii) are inert under elevated temperatures, mechanical influences or alkalinity; (iii) inhibit greying and dye transfer; (iv) help in formulation of high performance, low cost, eco-friendly phosphorus free detergents; (v) remove hardness from wash water; (vi) have high liquid absorption capacities and (vii) free of legislative restrictions.

Zeolite A is now a builder leading to compact and super compact detergents.

*Table 3.*

| Constituent | Composition (weight %) | |
|---|---|---|
| | Traditional | Compact |
| Surfactants | 10-15 | 10-25 |
| Builders (phosphate or zeolites) | 28-55 | 28-48 |
| Bleach | 10-25 | 10-20 |
| Bleach activator | 1-2 | 3-8 |
| Fillers (sodium sulphate) | 5-30 | None |
| Corrosion inhibitors | 2-6 | 2-6 |
| Enzymes | 0.3-0.8 | 0.5-2.0 |
| Fluorescent brighteners | 0.1-0.3 | 0.1-0.3 |
| Foam controlling agents | 0.1-4.0 | 0.1-2.0 |
| Perfume | Trace | Trace |
| Water | to 100% | to 100% |

## Cobuilder

Organic polymers (polycarboxylates) are added as cobuilders to make the zeolite work more effectively. Cobuilders include poly(sodium carboxylates) consisting of neutral or ionic allyl glycoside monomer and maleic acid or itaconic acid comonomer and poly (allyl-$\beta$-D-glucofuranosiduromic acid-co-maleic acid). Sodium carbonate is added to raise the pH as the zeolite works better at high pH.

## Additives for Secondary Benefits

i) Sodium carboxymethylcellulose is a cellulose derivative of which 0.4 –1.5 hydroxyl groups are linked to -$CH_2COONa$ moie-ties (molecular weight range between 20,000 and 5,00,000). This polymer improves the soil suspending power of detergent and prevents redeposition of soil on cotton.

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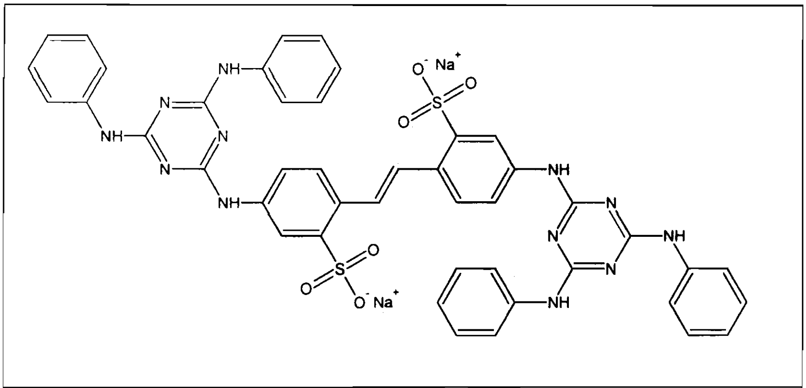
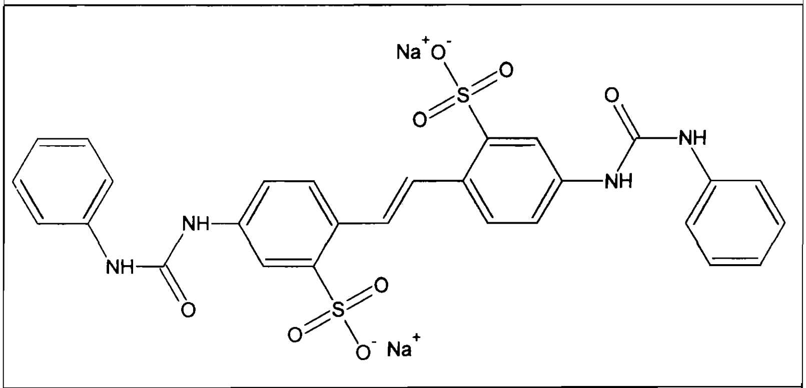
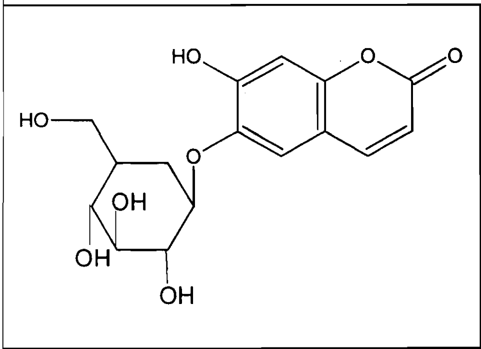
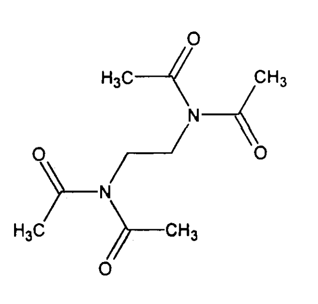
ii) Derivatives of 4,4'-diaminostilbene disulphonate (*Figure* 1). Phenyluriedo derivatives of 4,4'-diaminostilben-2,2'-disulphonic acid (*Figure* 2) and natural coumarin derived from esculetin (*Figure* 3) are examples of fluorescent whiteners. They adsorb on the fabric like dyes but they absorb ultra violet light (normally present in sunlight) and re-emit radiation in the blue part of the spectrum thus brightening the fabric.









TAED

*Figure 1. (top)*
*Figure 2. (center)*
*Figure 3. (Bottom left)*
*Figure 4. (Bottom right)*

iii) Sodium sulphate is added to make the material flow freely. Alcohols are added to liquid detergents to keep everything in solution. Borax is used as a filler to absorb water and produce free-flowing powders.

iv) Sodium percarbonate ($2Na_2CO_3.3H_2O_2$) and sodium perborate ($NaBO_3.3H_2O$), in combination with bleach activator like tetraacetylethylenediamine (TAED, *Figure* 4) are used for bleaching at low temperature of ~ 35°C.

v) Sodium silicate ($Na_2O$. x $SiO_3$; x = 3-5) is added to reduce the corrosion inside the washer.

vi) A small quantity of ordinary soap suppresses foaming, which is undesirable in washing machines.

vii) Sometimes colouring agents are added to improve the appearance and the fragrances to mask the odors of other ingredients. These serve also to provide brand identity.

## Fabric Softeners

Fabric softeners provide secondary washing benefits. They impart softness by controlling static electricity. The active ingredients are cationic surfactants such as

di-n-alkyldimethylammonium chloride (n- alkyl = n - $C_{14}$, n - $C_{16}$ and n $C_{18}$), $[CH_3(CH_2)_{15}]_2 N^+ (CH_3)_2 Cl$ (II)

or the more readily biodegradable esterquat

$$[CH_3(CH_2)_{15}C(O)O\,CH_2CH_2]_2 N^+(CH_3)(CH_2CH_2OH)(CH_3SO_4^-) \quad \text{(III)}$$

These compounds adsorb on cotton and cationic head groups bind to the carboxylate anions on the surface of the cloth. The alkyl chains form a fatty monolayer which lubricates the cotton fabric and thus prevents friction damage to the fibers, thereby giving a pleasant feel. Softness also reduces water retention after spinning and thus less energy is needed to dry the clothes.

## Enzymatic Detergents

Enzymes are established ingredients in powder, liquid and tablet detergents all over the world.

Enzymes are established ingredients in powder, liquid and tablet detergents all over the world. In 1913, Otto Rohm's patent indicated the use of crude presoak pancreatic enzyme detergent as washing aid for laundry cleaning. Over the years, several new and better enzyme preparations have emerged for use in detergents, such as alkaline protease and amylase in mid 1960s, cellulase in 1985 and lipase in 1988. Various enzymes used in detergents are summarized in *Table* 4.

| Enzyme | Substrate | Source/Production |
|---|---|---|
| Protease (mainly non-specific serine endoprotease hydrolyzing carboxyl side of hydrophobic amino acid and most peptide links) Biodegradable | Protein based stains like blood, egg, milk, grass and sweat Not used to wash wool or silk garments due to protein based fibres. | Submerged or solid state fermentation using *Bacillus licheniformis* or *Bacillus amyloliquefaciens*. |
| Lipases Biodegradable | Oil or greasy stains e.g. butter, salad oil, sauces, cosmetic and lipstick. | *Pseudomonas glumae* and *Humicola lanuginose* with high performance |
| Amylases Biodegradable | Starch based stains e.g. gravy, potato, porridge, custard, pasta and chocolates. | *Bacillus licheniformis* usable at pH 10.5 and temperature of 85°C. |
| Cellulase Alkaline carboxymethyl cellulase Biodegradable | Microfibrils generated by continued use and repeated washings of only cotton garment. | *Aspergillus niger* *Trichoderma reesei* *Trichoderma viride* *Humicola insolens* *Bascillus sphacricus JS1* and genetic engineering. |
| Synthetic enzymes (quaternary amines, e.g., alkyl dimethyl benzyl ammonium chloride is a powerful cationic catalyst and exists as $R_4^+ OH^-$ under alkaline conditions). Non-biodegradable. | Hydrolyze ester and amides present in residual fats, oils and proteins. Their presence in body can be dangerous since pH of blood is slightly alkaline. | Deprived from quadernary ammonium compounds |

***Table 4. Enzymes used in detergents.***

In general, enzymes in detergents break down a large stain into smaller pieces of the same stain. Enzyme granules are usually included in commercial detergent powder at a concentration of 0.02 to 1 per cent. Enzyme liquid and slurry contain between 2 to 5 per cent enzyme protein and these are included in detergent powders at a concentration of 0.2 to 1 per cent. The maximum amount in granules, liquid and slurry is 0.05 per cent by weight in finished products. The enzyme activity (expressed as Glycine Units (GU) or Anson Unit (AU) varies from 1200 -1800 kGU/g in granulate, whereas from 1800-4200 kGU/g in case of liquid and slurry. Currently, the use of dual enzymes and tri-enzymes powder in detergent formulation is preferred, where the enzymatic hydrolysis and breakdown can be achieved considerably in comparison to single enzyme approach.

### *Advantages of Enzymatic Detergents over Non-enzymatic Detergents*

Enzyme detergents require low workable temperature and low mechanical energy; are cost effective, eco-friendly, less toxic, non-corrosive and have enhanced stability in different formulations, as compared to the non-enzymatic detergents.

***Applications of Enzymatic Detergents are as follows:***
(i) in medical field for cleaning of reusable medical instruments, as anti-corrosive agents and as lens cleaner;

(ii) in food and dairy industries, for cleaning of the ultra filtration and reverse osmosis membranes used for concentration, clarification and sterilization of liquid foods like skim milk, whey, egg white, fruit juices and beverages; and

(iii) for cleaning delicate Chinaware as they prevent the erosion of design and colours.

## Future Perspectives

Enzymes in detergent formulations are yet to reach their full potential. There is scope for the use of enzymes like lipoxygenase, glucose oxidase and glycerol oxidase for generating hydrogen peroxide *in situ.*

In our opinion, enzymes in detergent formulations are yet to reach their full potential. There is scope for the use of enzymes like lipoxygenase, glucose oxidase and glycerol oxidase for generating hydrogen peroxide *in situ*. Added peroxidases may aid the bleaching efficiency of this peroxide. These enzymes will have an edge over the routine bleaching agents used in detergent formulations. A great deal of research is currently in progress to develop lipases, which will work under alkaline conditions as fat stain remover. The shift towards non-ionic surfactants is expected. The use of additives including acrylate polymers and sodium perborate monohydrate may increase. The future development should focus on the use of surfactants based on reusable raw materials such as sugar and vegetable oils rather than oil-based material. The emphasis on compact detergents will reduce the consumption of sodium sulphate used as bulking agent. New eco-friendly formulations containing zeolites and enzymes would continue to be developed.

## Suggested Reading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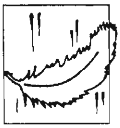

He was first of all a spontaneous person, following that a scientific genius, next an artist close to the creative spark, and only in the last instance, out of a feeling of duty, a 'homo politicus'.

*– Carl Friedrich von Weizsäcker on Werner Heisenberg*

Heisenberg was certainly not a political person, but he was forced to act on a political basis.

*– Elisabeth Heisenberg née Schumacher*