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**REVIEWS**

# Development of Surfactants and Builders in Detergent Formulations

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**Abstract** Surfactants and builders are the two most important ingredients in laundry, household and personal-care cleaning products. They play a key role in washing processes. The development of various surfactants (*e.g.*, anionic, nonionic, cationic, zwitterionic, and silicone surfactants) and builders (inorganic, organic and polymeric builders) used in the detergent compositions are reviewed and their detergency performance and biodegradability are discussed. In the future, the development of the surfactants and builders used in detergent compositions should be based on economic and environmental considerations. The use of the eco-friendly surfactants and builders derived from inexpensive renewable resources (*e.g.*, alkyl polyglucosides and bio-based polyesters) in detergent compositions is the developing trends in detergent industry.
**Keywords** detergent, surfactant, builder, detergency performance, biodegradability

## 1 INTRODUCTION

A laundry detergent composition generally comprises six groups of substances: surfactants, builders, enzymes, bleaching agents, fillers and other minor additives such as dispersing agents, fabric softening clay, dye-transfer inhibiting ingredient, and optical brighteners. Laundry detergents and, household and personal-care products account for over half the use of surfactant[1]. Therefore, the demand of the detergent industry is a driving force for the development of related chemical industry and chemical engineering which involve synthesis and production of surfactants and polymer builders. In this article, we will introduce the surfactants and builders frequently used in detergent compositions and discuss their development in the past, present, and future. The other ingredients in detergent formulations will be dealt with in a forth-coming paper.

## 2 SURFACTANTS

Surfactant is an abbreviation for surface active agent, which literally means active at a surface [2]. Surfactants are the single most important ingredients in laundry and household cleaning products, comprising from 15% to 40% of the total detergent formulation [3]. According to the polar head group, surfactants used in detergent formulations can be classified into four groups: anionics, nonionics, cationics, and zwitterionics. Nowadays, laundry detergents often contain a certain mixture of different types of surfactants to strengthen their cleaning performance capability and to remain mild to the skin of hands. Even though, we will mainly review the surfactants used in detergent formulations by group in this section, and will give some discussions on compositions containing a combination of different groups of surfactants at the end of this section.

### 2.1 Anionic surfactants

Anionic surfactants are used in greater volume than any other groups due to their ease and low cost of manufacture. The first surfactant is soap, which is made from a fatty acid such as animal fat or vegetable oil that is allowed to react with an alkali. It was the only choice of surfactant until the 20th century. Over the past 70 years, the anionic surfactant market for detergents has changed from soap to synthetic linear alkyl benzene sulfonate (LAS) [3]. Fig. 1 shows the structures of some major anionic surfactants used in detergent compositions. The preferred counterions of the anionic surfactants are sodium, potassium, lithium, ammonium and alkylammonium, especially sodium.

Soap is obviously a sustainable surfactant and shows excellent performance under the appropriate conditions. However, it is sensitive to hard water and does not work well at lower temperatures, including cold water. These shortcomings have been a major driving force for the development of synthetic anionic surfactants. The time interval between entry and exit of each main anionic surfactant is plotted in Fig. 2. Natural alkyl sulfates were first introduced in laundry detergents around 1932. Then, the low-cost surfactant called alkyl benzene sulfonates became the work-horse among synthetic surfactants. Originally, branched-chain alkyl benzene sulfonates (ABS) were used in detergent compositions, but microbes could not break down ABS and thus they left foam in river water. They were replaced by linear alkyl benzene sulfonates (LAS) such as sodium dodecybenzene sulfonate and sodium xylenesulfonate, which are readily biodegradable. In today's market, LAS is still a key low-cost surfactant and alkyl sulfates (AS) are simultaneously in use [2, 3].

It is known that an LAS surfactant will be sequestered and be precipitated from wash solution by divalent cations under high water hardness conditions, reducing the cleaning power of the detergent. The use of low levels of alkyl ethoxy ether sulfate (AES) surfactant in a surfactant system substantially reduces the tendency of the anionic surfactant to precipitation under high wash-water hardness [4]. Alpha olefin sulfonate (AOS), which is one of the anionic surfactants

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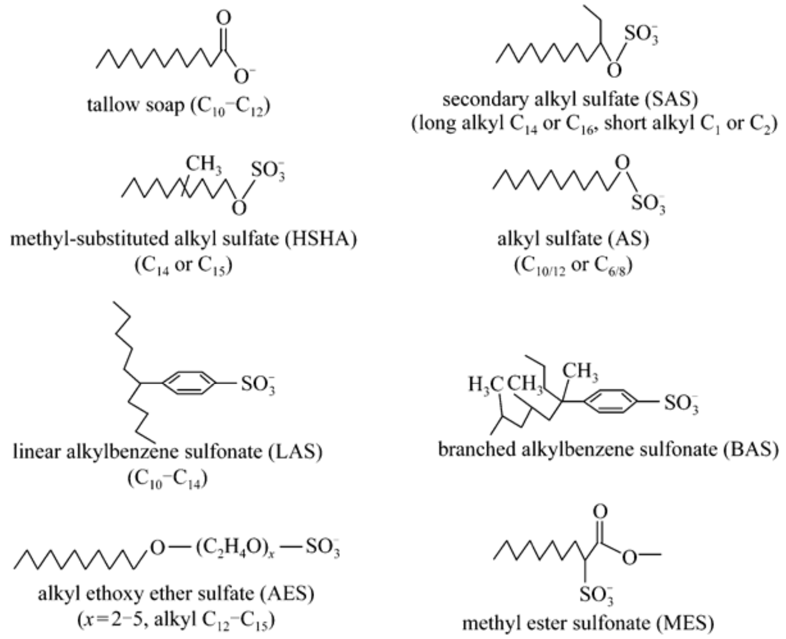


**Figure 1 Structures of some major anionic surfactants in detergent compositions**

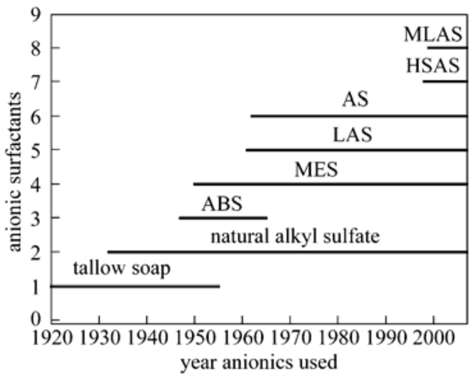


**Figure 2 Evolution of some major anionic surfactants [3]**
HSAS—highly soluble alcohol sulfate; MLAS—modified linear alkyl benzene sulfonate

that is fast gaining acceptability in detergents due to its superior performance characteristics and enhanced biodegradability, may play a function similar to AES. Suri *et al*. [5] found that the binary surfactant system of LAS and AOS exhibited minimal surface tension and minimal critical micelle concentration at the surfactant ratio of 80∶20, indicating synergism in mixed micelles under this condition. The mixed micelles improve hard-water tolerance of LAS and reduce precipitation of LAS by calcium, resulting in superior detergency, low ash deposit and better stain-removing ability when compared with products containing LAS as the sole active surfactant.

To overcome the precipitation of LAS surfactant in hard wash-water, two other aspects attempts have been carried out. On the one hand, Cripe and his colleagues [6–8] have discovered mixtures of mid-chain methyl-substituted alcohol sulfate surfactants called highly soluble alcohol sulfates (HSAS). It allows for the use of long-chain alcohols, such as $C_{14}$–$C_{17}$, in laundry detergents under today's cold- and hard-water environments. HSAS is extremely tolerant to calcium and has better surface activity and solubility than AES and AOS surfactants. On the other hand, Scheibel *et al*. [9, 10] synthesized a modified linear alkyl benzene sulfonate (MLAS), which has a high solubility in the presence of calcium compared with the current LAS. Besides, the MLAS has a favorable biodegradability and toxicity profile compared with the most used LAS [11].

It has also been discovered that a particular sub set of the class of secondary alkyl sulfates (SAS), offer considerable advantages to the formulator and user of detergent compositions. They can be formulated as high surfactant particles for use in granular detergents and dry-mixed into granular detergent compositions without the needs for the spray-drying process [12]. It has been confirmed that the agglomerated SAS particles provide a significantly improved solubility of the granular detergent and thus can be used in laundry detergents especially under the cold water washing conditions.

AS, AES, and LAS are all high production volume and down-the-drain chemicals used globally in detergent and personal care products, preferentially adsorbing to sediments. Sanderson *et al*. [13] studied the risk caused by AS, AES, and LAS in river water and sediments, and it was concluded that AS, AES, and LAS resulted in low aquatic risk.

Alkyl ester sulfonates, especially methyl ester sulfonates (MES), are environmentally friendly anionic surfactants, which have the potential to biodegrade faster than LAS. MES has been produced largely or entirely from renewable, non-petroleum raw materials and applied to detergents and cleaning products by companies such as Lion Corporation, Stepan and Malaysian Palm Oil Board [14]. Since its Krafft temperature is high, MES itself does not offer the desired levels of overall cleaning performance, especially in the area of grease/oil cleaning. Effective solutions include adding a hydrotrope or mixing it with other surfactants that possesses a lower Krafft temperature [15]. Murch and Mao [16] discovered that the use of MES in combination with certain polyhydroxy fatty acid amide surfactants improved the detergency. If crude oil prices continue to remain high, MES may reach usage volumes comparable to AS, AES, and LAS.

Other anionic surfactants used in detergent compositions are sodium alkyl glyceryl ether sulfonates, di-anionic surfactants such as disulfonates and disulfates [17], and anionic gemini surfactants [18]. In contrast to monosulfonated surfactants such as LAS, disulfonated surfactants such as alkyldiphenyl oxide disulfonate exhibit excellent solubility in the presence of divalent counterions. The compositions containing low levels of di-anionic cleaning agent provide outstanding results of greasy/oily soil removal and whiteness [19]. The alkyldiphenyl oxide disulfonate provides better detergency performance than LAS over a broad range of washing-water hardness whereas its toxicity to fish is consistent with LAS when it is added directly to the effluent [20, 21].

## 2.2 Nonionic surfactants

Nonionic surfactants have been extensively used in the area of the laundry detergents and personal-care formulations in combination with anionic surfactants. The nonionic surfactants are represented mostly by linear alcohol ethoxylates, with the alcohols being derived from either petrochemical raw materials or natural resources. They include alcohol ethoxylate (AE), alkylphenol ethoxylate (APE), methyl ester ethoxylate (MEE), ethoxylated amine, ethoxylated amide, alkyl polyglycoside (APG), polyethylene oxide-polyalkylene oxide diblock copolymer, *etc*. The structures of main nonionic surfactants used in detergent formulations are given in Fig. 3. Different from anionic surfactants, the detergency of compositions containing nonionic surfactants is not sensitive to hard water since no precipitation occurs in the presence of divalent ions. Furthermore, nonionic surfactants can be used to deterge animal fibers such as silk and wool, to avoid the ionic adsorption of surfactant on the amino groups in the fibers since electrostatic force does not work for nonionic surfactants.

APEs such as nonylphenol ethoxylates are efficient, cost effective versatile products which have been used widely in detergent compositions for over forty years. They have a better detergency performance than alcohol ethoxylates (AE). They meet the primary biodegradability but the metabolic products resulting from the degradation process do not readily degrade further and may have undesirable side effects on aquatic life [22].

AE has a higher detergency than anionic surfactant LAS when they are used alone. The aquatic toxicity of AE increases with a reduction in the degree of ethoxylation and with an increase in the alkyl chain length of the hydrophobe. From the experiments by Belanger *et al*. [23], low levels of risk were inferred for AE in the aquatic environments of Europe and North America. Secondary alcohol ethoxylates [24] have almost the same biodegradability as that of primary AE, but show higher detergency and slightly lower toxicity. They have a high liquidity and therefore the dry-mixing method is favored over the spray-drying method to manufacture detergent powder containing secondary alcohol ethoxylates. Investigation has shown that methyl ester ethoxylates (MEE) has a similar soil removal but a better bio-degradability in comparison with AE. When used in laundry liquid detergents, MEE should be easier to handle than AE because of their reduced tendency to form gel [25].

With the improved understanding of the effect of the structure of ethoxylates on aquatic toxicity and

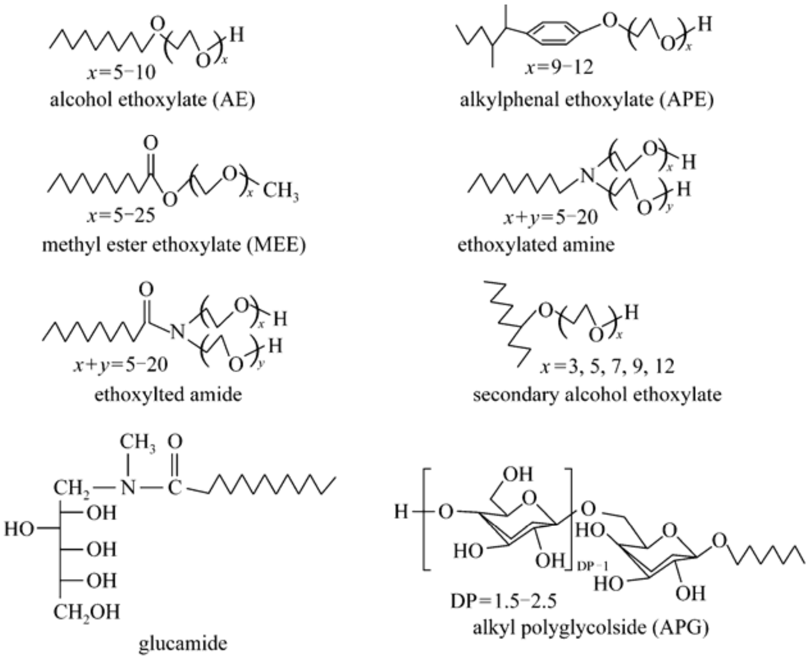


**Figure 3 Structures of some major nonionic surfactants in detergent compositions**

biodegradability, it has been possible to develop products which meet both requirements of detergency performance and environmental effects. For example, Scardera and Grosser [26] discovered an alkali-stable nonionic surfactant product which has the formula of $RO(CH_2-CH_2-O)_a-[CH_2-CH(R')-O]_b-H$, where $a=9$–15, $b=3$–5, R is a linear alkyl hydrocarbon having an average of approximately 16 to 18 carbon atoms, and R′ is methyl or ethyl. This kind of surfactants are biodegradable, are water-soluble, moderate to high sustained foaming, and are stable on dry caustic, making them useful in particular alkaline compositions, such as detergent formulations. Block copolymers of ethylene oxide (EO) and propylene oxide (PO) may improve grease removal when incorporated into liquid dishwashing detergent compositions and as anti-redeposition agents in powder detergent compositions [27]. They are also useful in the removal of oily soils from fabrics [28]. Hashimoto and Tonegawa have recently disclosed a composition containing a surfactant with structure of $RO(AO)_n(EO)_mH$, where $n=0$–5, $m=1$–20, R is $C_8$–$C_{10}$ alkyl, and AO is $C_3$–$C_4$ oxyalkylene. This composition is useful in scrubbing hand cleaners, hand soaps and face cleansers with low skin irritation, and shows good oily soil-removing properties [29].

For ethoxylated amines, detergency performance depends on the hydrophobe and on the number of moles of ethylene oxides attached. The cocoamine with 5 mol EO and tallowamine with 10 mol EO have shown the best detergency performance. Ethoxylated amines should be better surfactant than AE since besides their good detergency they show good performance as dye-transfer inhibitors in combination with nonionic surfactants. They can be used to formulate a variety of cleaning products for both household and industrial purposes. The only drawback is their higher price. Commercial ethoxylated amines cost between 20% and 100% more than AE depending on chain length and amount of EO.

Ethoxylated amides, especially for tallowamide, are very cost-effective nonionic surfactant. They also possess both dye-transfer inhibition properties and the detergency performance of the other commonly used surfactants in liquid laundry formulations such as AE. However, they can be dark in color.

The development of surfactants based on carbohydrate and vegetable oils is the result of the product concept based on the exclusive use of natural resources. Sugar-based surfactants are gaining increased attention due to their advantage with regard to performance, health of consumer and environmental compatibility compared with some standard products [30]. Among all the sugar-based surfactants, APG and glucamides have gained considerable importance over the past few years. Both types of surfactants show synergistic effects with primary anionic surfactants and have low irritation potential due to their polyhydroxy structure. They are not considered as toxic or harmful in acute toxicity tests but in high concentration have to be classified as irritating to the skin and eyes. APG is used extensively as a co-surfactant in dishwashing detergents, heavy-duty powder detergents and personal-care products. Experiments have indicated that APG with an alkyl chain length of $C_{12/14}$ was preferred for laundry detergents and gave better detergency for particulate soil and motor oil soil [31].

Hreczuch [32] has examined the possible use of ethoxylation product of low-erucic rapeseed oil acid methyl esters as a nonionic surfactant, which is gaining more and more interest in the market. They are easy to formulate into attractive liquid detergents with high cleaning performance and show a more favorable eco-toxicological profile compared with fatty alcohol ethoxylates [33]. Kharkate *et al*. [34] synthesized an alkyd resin polymeric surfactant based on soybean oil and rosin. This polymeric surfactant is suitable for liquid detergent formulation in association with sodium lauryl sulfate and can be used as a substitute of LAS. The prepared compositions of liquid detergents have equivalent detergency performance compared with the commercial ones, but are more economic and eco-friendly.

### 2.3 Cationic surfactants

The majority of cationic surfactants used in detergent compositions are based on the nitrogen atom carrying positive charge. In general, the preferred solubilizing anion is a halide or methosulfate ion. Quaternary ammonium compounds (quats), especially dioctadecyl dimethylammonium chloride are used as antistatic agent due to its high antistatic activity. The quaternary ammonium and ethoxylated quats, are used as a common fabric softener [35]. It works by reducing the friction between fibers, and between fibers and the skin, and thus it can also be used as hair conditioners. Kennedy *et al*. [36] described a method for imparting mildness properties to a cosmetic cleansing composition by adding a minor proportion of an alkyleneoxylated bisquaternary ammonium compound. However, hydrolytically stable cationic surfactants show higher aquatic toxicity than most other classes of surfactants. Ester quats, which are a new type of environmental friendly cationic surfactants, have been used to replace dialkyl quats as textile softening agents. The structures of some types of quats are shown in Fig. 4.

It has been found that addition of ethoxylated quats to floor and stone cleaners enhances the spreading and drying abilities and, the lime soap dispersing and emulsification properties. This made the cleaners more effective on slip resistant surfaces, leading to a reduced time consumption for washing those floors and stones [37].

It has been also found that detergent compositions containing quat salt and low levels of iminodisuccinate (IDS) or hydroxyiminodisuccinate (HIDS) exhibited improved soil and stain removal in conjunction with reduced fading of dyes on colored fabrics [38]. Recently, Hsu *et al*. [39] have discovered that the polyanionic ammonium surfactants, which are quaternary ammonium salts with alkyl sulfate or alkylbenzene sulfonate anions as counterions, exhibited characteristics different from cationic surfactants and showed substantially better performance in soil removal than the physical mixture of anionic surfactants and polyamines. The presence of polyanionic ammonium

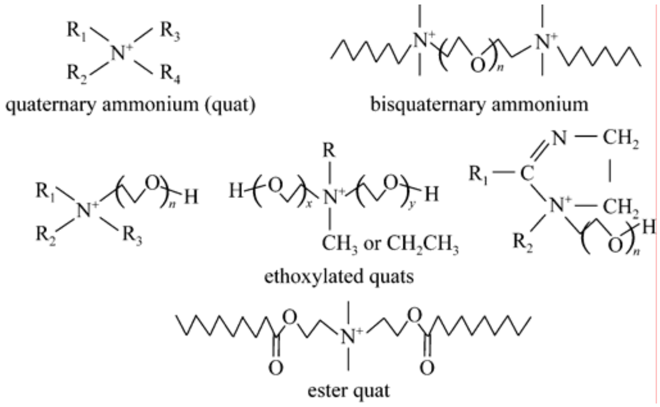


**Figure 4 Structures of major cationic surfactants in detergent compositions**

surfactant in a detergent formulation greatly improves the deposition of fluorescent whitening agent onto a fabric to enhance the whiteness.

## 2.4 Zwitterionic surfactants

Zwitterionic surfactants contain two charged groups of different signs under normal conditions. One main type of zwitterionic surfactants is the amphoteric surfactant, which can be either cationic, zwitterionic, or anionic, depending on pH of the solution [2]. The structures of the main zwitterionic surfactants used in detergent compositions are shown in Fig. 5.

Amphoteric surfactants such as betaines and sulfobetaines, are widely used in washing products including household, personal-care detergents, *etc* [40]. The detergency on oily soils and biodegradability of betaines are better than that of AE. The cleaning of betaines or sulfobetaines is much better when the nonionic surfactant is used with the amphoteric. However, the amphoteric surfactants are generally mild, with lower skin and eye irritation when compared with the commonly used anionic and nonionic surfactants. They can be incorporated into detergent composition in order to thicken the composition without using a thickener, provide excellent temperature stability, and improve the mildness on the skin. This composition thus is particularly suited for washing skin and hair, especially face [41]. Betaines can be used in the industrial and institutional detergents because of their extreme pH stability. In fabric softener formulations, betaines can be used as dispersing agents for the quat. They can also be used in laundry detergents as dye transfer inhibitors for acidic and direct dyes. Betaine, sultaine or preferably their mixture in the composition containing anionic surfactant mixture can provide thickening and high foam property to the soap. They are foam boosters and thus improve foaming of the soap [42].

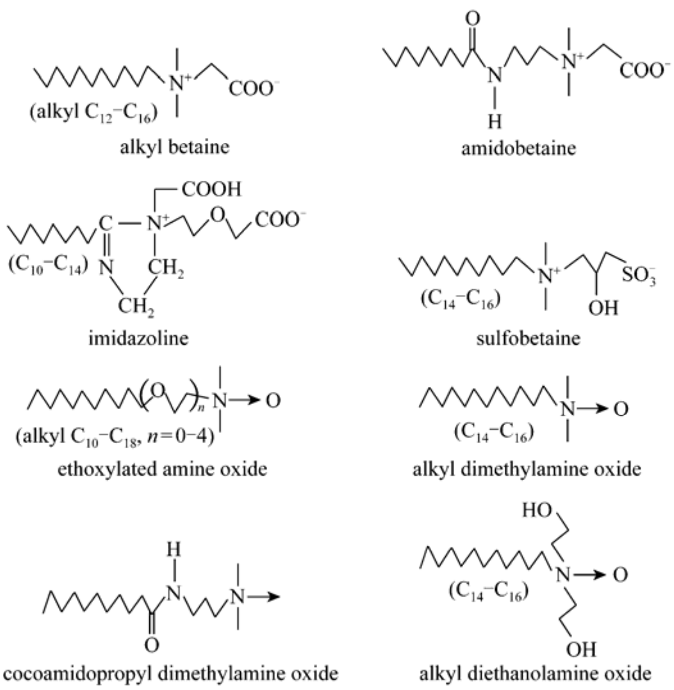


**Figure 5 Structures of some major zwitterionic surfactants in detergent compositions**

Amine oxides such as lauryl dimethylamine oxides are similar to betaines. In acid solutions, the amino group gets protonated and the amine oxide acts as a quat whereas in alkaline solution, it behaves as a nonionic surfactant. Amine oxides exhibit good soil removal properties, particularly the greasy oil removal properties and can be used in laundry detergent, fine-fabric wash, and laundry prespotter formulations. Amine oxides are also good foaming agents, foam boosters, and stabilizers for anionic surfactant [43]. They can act as dye-transfer inhibitors for certain dyes. They are one of the best types of surfactants for use with chlorine bleaches due to their resistance to oxidation [44].

### 2.5 Silicone surfactants

Silicone surfactants have been used in cosmetic formulations for more than half a century. There are two basic structures of silicones: linear and cyclic polydimethyl silicones as shown in Fig. 6, where R is the modifying group. Linear polydimethyl siloxanes give a very silicone specific silk-like feel on skin and hair when applied to skin- or hair-care formulations. Eight- and ten-membered cyclic derivatives also have widely used in cosmetic formulation. On the one hand, the cyclic silicones are able to improve smoothness and softness of the skin as well as hands, combing characteristics and glossiness of treated hair, but the effect is only temporary due to their volatility. On the other hand, linear polydimethyl siloxanes, though non-volatile, are insoluble in water and poorly compatible with cosmetic oils. Fortunately, the substitution of methyl groups in polydimethyl siloxanes by quaternary or amphoteric groups may lead to the products of siloxanes with improved substantivity which are mostly used in hair-care products [45].

The detergent composition comprising a source of alkalinity with a combination of polyethylene oxide condensates of alkyl phenols and a polydimethyl siloxane results in surprisingly effective removal of hydrophobic waxy-fatty soil such as lipsticks soils from the surface of ware. The combination of the two surfactants reduces surface tension between the soil and the ceramic or siliceous surface of glassware or tableware [46].

Before concluding Section 2, we would like to mention that most detergent formulations use a combination of various surfactants [47] to balance their performance. A combination surfactant system usually exhibits better detergency performance than the composition containing single-surfactant. Therefore, one or more anionic, one or more nonionic, one or more zwitterionic, and even one or more cationic surfactants are generally used in a formulation. Various combinations of surfactant systems have been disclosed for detergent compositions of different uses [4, 48].

## 3 DETERGENCY BUILDERS

Surfactant efficiency is greatly reduced in hard water and surfactants do not show good performance even in softer water. Furthermore, large amounts of surfactants in detergents not only significantly increase biological demand in water but also impose heavy load on sewage works and on the environment due to their eco-toxicity. To remove $Ca^{2+}$ and $Mg^{2+}$ ions existing in hard water and in soils, and thus to lower the content of surfactants in the detergent formulations, detergency builders are often used in conjunction with surfactants. A potential builder should satisfy a large number of requirements including sequestering ability, alkalinity, buffer capacity, bleach compatibility, soil deflocculation, oral toxicity, skin absorption, eye irritation, effects on fish and other aquatic animals, and other environmental and economic practicability [49].

### 3.1 Inorganic builders

Sodium tripolyphosphate (STPP) meets the essential requirements of a builder and therefore it was the most widely used builder in the past. In addition to its great capacity to remove the $Ca^{2+}$ and $Mg^{2+}$ ions presented in hard water and in soils, STPP facilitates dissolution of detergents, maintains alkalinity during washing, prevents dirt reposing on fabrics by suspending it in the wash-liquor, and protects the washing machine against corrosion. STPP shows efficiently performance under all washing conditions. Thus far, no other single chemical offers even most of the different properties of STPP. Anhydrous STPP exists in polymorphic and monoclinic forms known as high-temperature Form-I and low-temperature Form-II [50]. Their physical properties and hydrolytic degradation in solution have been extensively investigated during the 1950s and 1960s [51–54]. Compared with Form-II, Form-I exhibits a higher hydration rate; therefore, it cements together and sometimes solidifies

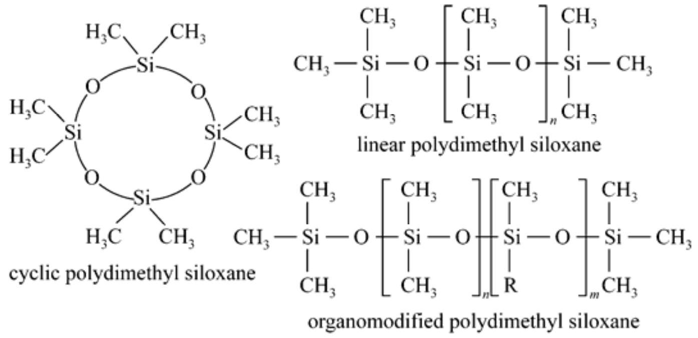


**Figure 6 Structures of polydimethyl siloxanes and their derivatives**

after addition of water, causing serious problems in the manufacturing of washing powders with the use of spraying dryers. In modern technology, it is possible to adjust the From-I/Form-II mass ratio, granular size, color, *etc*., according to the requirements of consumers by mixing Form-I with Form-II [50].

However, phosphates are excellent fertilizer for algae, bacteria, and other flora and fauna in rivers, lakes and oceans, making them bloom at very rapid rates, exhausting the oxygen supply both in the surface and in the bottom layers of water bodies, and killing fish. This phenomenon is called eutrophication [55]. The phosphorus content originated in detergents is 50%–60% in domestic waste water; the remainder is from human waste and agricultural runoff. Though removal of phosphates from sewage in treatment plants could eliminate 80%–95% of all phosphorus, the cost is considered too high to allow immediate and general application [49]. Replacing phosphate builders in household detergent formulations may reduce the phosphorus concentration of effluents entering rivers and lakes. Subsequently, other water softeners such as sodium carbonate, sodium silicate and ethylenediaminetetraacetic acid (EDTA) were used as a substitute for STPP. Although sodium carbonate- and sodium silicate-built detergents show almost the same performance as the leading phosphate formulations, their high alkalinity is harmful to our skin and eyes. In addition, they produce deposits on fabrics which trap dirt, provide a breeding ground for bacteria, and cause washed fabrics to become harsh, grey, and to wear out more quickly.

Borates are another group of common constituents of many types of detergents. Although the borate is primarily intended to serve as hydrogen peroxide bleach, in many cases it functions similar to detergency builders. Greenhill-Hooper [56] examined and compared the builder performances of borate with those of other common builders such as STPP and sodium carbonate. Except for its relatively weak $Ca^{2+}$ ion sequestration capacity, the experiment demonstrated that borate showed good performance similar to a builder. Borax solution has a pH of approximately 9.13 at 313 K, which is able to maintain alkalinity within an optimum pH range (9–10.5) for good detergency. Besides, borate is able to lower interfacial tension between oil and water, and enhance the surface charge characteristics of clay and oxide soils suspended in solution. The experiment also indicated that borate showed better detergency performance of pigment and oily soils in hard water than carbonate did. Sodium perborate, for example, removed pigment and oily soils from fabrics more easily than sodium carbonate did.

Nowadays, zeolites, particularly zeolite A (a sodium aluminium silicate) are used in phosphate-free detergents, necessarily in conjunction with other builders such as polycarboxylates or nitrilo triacetic acid, EDTA and sodium carbonate. The experiments carried out by Maki and Macek [57] demonstrated that zeolite A was nontoxic at projected environmental levels to aquatic series representing three major trophic levels of freshwater and marine aquatic communities, and that it did not contribute to the eutrophication potential of surface waters. Thus, zeolites have beneficial effects as eco-friendly detergent builders due to growing public sensitivity to environmental issues and the resulting ban on the use of STPP. Zeolite A possesses a good ion exchange capacity for the $Ca^{2+}$ ion in hard waters and soils, and its performance is enhanced in concentrated detergent formulations due to the lower total salt normality and lower background level of $Na^+$ ions [58]. However, the absorption rate of zeolite A is much lower than STPP, and a small ion exchange capacity is found for the $Mg^{2+}$ ion [59, 60]. Consequently, other zeolites, such as zeolite 13X [61], zeolite P [62] or clinoptilolite [63], have been reported for use in detergent formulations. The detergency experiments of Culfaz *et al*. [64] showed that zeolite A and zeolite X were more effective in cleaning than STPP and clinoptilolite at low temperatures, while all these builders had same effectiveness at high temperatures. LAS appears to be the most suitable for use with clinoptilolite and the addition of EDTA as a co-builder will improve the performance of clinoptilolite.

The use of zeolites increases suspended solids and may cause fouling of pipeline. It significantly increases sludge volumes in sewage treatments plants, making disposal of sludge more difficult. In addition, the surfactant in the zeolite detergent is trapped inside the zeolite and takes time to diffuse into the wash liquor. To compensate for the shortcomings as a detergent builder, an alkaline compound such as soda ash or sodium silicate is added.

To manufacture more compact powder detergents and more ecological detergents, a multifunctional builder is demanded. Layered crystalline silicate ($Na_2Si_2O_5$) is a promising candidate since it combines a high performance per unit mass with a high degree of multi-functionality [65]. This new builder is composed of a δ phase of sodium disilicate $Na_2Si_2O_5$, which possesses a polymeric layered bidimensional crystal structure as well as small amounts of α and β phases as impurities [66]. It can be synthesized from either a sodium silicate solution [66] or an amorphous silicate [67]. Its advantages over zeolite A lie in its water-solubility and good ion-exchange capacity for $Mg^{2+}$ ions. The solubility of the δ phase of sodium disilicate in deionized water is higher than that in tap water because of its retention capacity while similar solubility is found for the α phase in deionized and tap waters, indicating that the α phase has much lower retention capacity for both $Ca^{2+}$ and $Mg^{2+}$ ions [68, 69]. Because the δ phase of sodium disilicate is water soluble, it contributes very little to sludge formation in wastewater treatment plants and partially buffers the alkalinity of the water liquor. Besides, it has a corrosion-inhibition action and can be mixed with any other builder, being used in formulations of both liquid and highly compact detergents. All these advantages make it a good builder for P-free detergents. Last but not least, it is more expensive than zeolite A, but considering the costs involved in the total zeolite builder system, it is economically comparable to zeolite [66].

### 3.2 Organic builders

Organic builders such as nitrilotriacetic acid

(NTA), ethylenediaminetetraacetic acid (EDTA), disodium 3-oxapentanedioate (ODA), iminodisuccinic acid (IDA), and sodium citrate (Na-C) are potential substitutes for the traditional detergent builders, especially for phosphates whose applicability is restricted due to their eutrophic effect on the environment. The calcium sequestering capacities (CaSC) of these organic builders are presented in Fig. 7. For comparison, CaSC value of STPP is also included in the figure. Except for sodium citrate, the organic builders have good calcium sequestering capacities. A crucial problem with respect to the organic builders is whether they would impose any adverse ecological or toxicological effects.

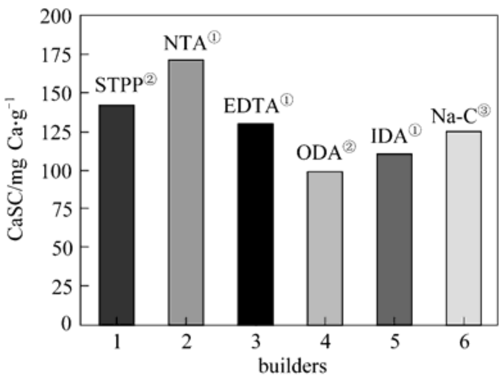


**Figure 7 Calcium-sequestering capacities (CaSC) of different organic builders**
①—Ref. [70] (pH=10, 298.15 K); ②—Ref. [71] (pH=9, 303.15 K); ③—Ref.[72] (pH=10, 303.15 K)

Sodium citrate has been used in some commercial P-free detergents. Although it is fully biodegradable and leaves no trace in the environment, its cost is high and its sequestering power is mediocre. The use of NTA as a builder in washing and dishwashing detergents leads to exposure levels that are more than $10^5$ times below toxicity risk levels, and does not cause skin or eye irritation. The potential environmental effects of NTA as a household detergent builder are heavy metal mobilization and toxicity to aquatic organisms. Due to the highly toxic chemicals used at the NTA producing stage, stringent safety requirements are needed [73]. NTA is banned or its use is restricted in several countries such as USA and Switzerland, which is attributed to its increased transmission of heavy metals. EDTA is very poorly biodegradable and has a similar disadvantage as NTA. The use of both EDTA and NTA are not authorized in detergents eligible for the European Union Eco-label.

It is discovered that hard-surface cleaning compositions, especially for automatic dishwashers, containing dextrin as builder component show performance equal to other similar compositions containing sodium citrate instead of dextrin [74].

Amino acid-*N*,*N*-diacetic acid salts or its derivatives (see Fig. 8) are biodegradable water-soluble co-builders used in liquid detergent or high-density granulated detergent. It is known that the use of one or more builders in a liquid detergent may reduce the solubility or clouding point of the surfactant as the

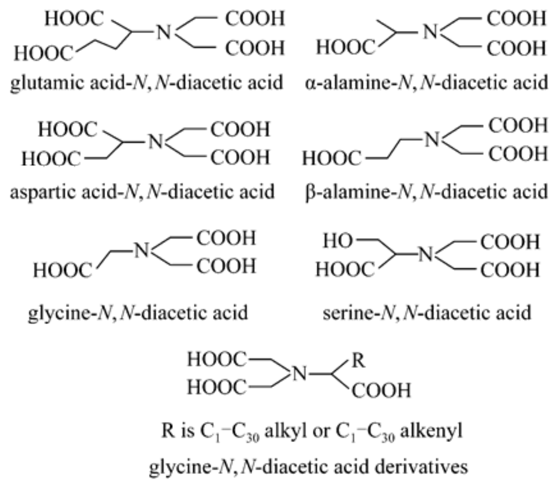


**Figure 8 Amino acid-*N*,*N*-diacetic acid and derivatives**

main agent and thus the compatibility is deteriorated, resulting in, *e.g.*, white turbidity or separation of the white turbid layer into two layers with the elapse of time. In order to prevent these and avoid an increase in the cost of transporting the detergent, an amino acid-*N*,*N*-diacetic acid salt or its derivative is introduced as a co-builder in the formulation to obtain a high concentration liquid detergent composition [75]. whereas, the use of an amino acid-*N*,*N*-diacetic acid salt or its derivative makes it possible to reduce the amount of insoluble ingredient in a high-density granulated detergent and therefore, to improve the solubility of the detergent, while the properties pertaining to its use are maintained or even improved [76, 77].

### 3.3 Polymer builders

Possible alternatives to STPP are water-soluble polyelectrolyte polymers. Polycarboxylates, such as homo- and copolymers of acrylic acid or maleic acid, show a marked superiority to STPP in their ability to sequester calcium ions, to prevent incrustation of fibers, and to re-dissolve calcium salt precipitates [49, 78]. Detergents containing the polymers derived from 2-sulfoacrylic acid or its salts show good resistance to environmental fouling while exhibiting good builder activity [79]. However, there is an environmental uncertainty with respect to these polycarboxylates, *i.e.*, they are not biodegradable and therefore persist in oceans, lakes and other water depositories if they are used as builders in detergent formulations. Consumers do not see these polymers washed up on beaches; their effects can be hardly visualized, making the problem more dangerous. To avoid further accumulation of recalcitrant substances in waterways, the commercial development of polymer builders is particularly needed [80].

Poly(amino acids) with free carboxylic groups, such as poly(aspartic acid) [81] and poly (glutamic acid), have both good biodegradability and necessary functionality similar to poly (acrylic acid), but the performance of these co-builder is not so good as that of the acrylic polymers. Poly(aspartic acid) polymers are most easily prepared by the thermal condensation of aspartic acid followed by the hydrolysis of the

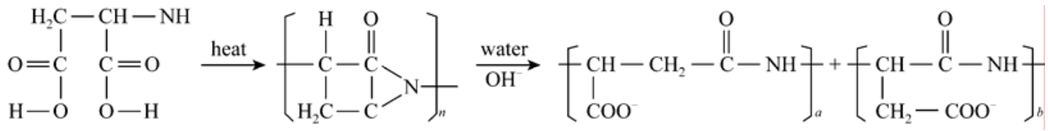


**Figure 9 Synthesis process of the thermal poly(aspartic acid)**

resulting poly(succinimide), as shown in Fig. 9. These polymers are more effective if the mole fraction of beta form is maximized, perhaps due to the structural similarity to poly(acrylic acid). Besides, the thermal and pH stability of these polymers are limited and the nitrogen, which is one of the major nutrients contributing to eutrophication, is transferred into the environment. Poly(malic acids), the polyester equivalent of poly(aspartic acid), may be useful polymers for detergents that are biodegradable. Modified starches that improve wash performance of detergents are being marketed.

An alternative way to prepare a biodegradable polymer is to introduce biodegradable segments into the main chain of the synthetic polymer. Biodegradation and builder performance tests indicated that the polymers prepared using this method with high biodegradable segment content showed better biodegradability, but poor builder effect when compared on an equal mass basis. The detergency can be improved greatly by increasing the amount of polymeric builder used in the detergent formulation [71, 82, 83]. Japanese researchers Matsumura *et al*. [82] selected the vinyl alcohol block as a biodegradable segment in the polymer chain and prepared two series of poly[(disodium fumarate)-co-(vinyl alcohol)] [p(FU-VA)] and poly[(disodium maleate)-co-(vinyl alcohol)] [p(MA-VA)] by copolymerization of vinyl acetate with dimethyl fumarate or diethyl maleate. Builder performance of p(FU-VA) and p(MA-VA) on an equal basis in a heavy-duty detergent formulation shows that the fumarate copolymer is more effective than the maleate copolymer, *i.e*., the detergency and calcium sequestration capacities of fumarate copolymers are better than those of maleate copolymers due to the conformation of their copolymers in aqueous solutions [82]. Sodium dicarboxyamylopectin (DCAp) [83] and sodium dicarboxyamylose (DCAm) [71] also belong to this kind of polymers. Experiments indicated that they were biodegradable in anaerobic as well as aerobic environments. DCAp with more than 70% dicarboxylation shows better builder performance than that of STPP. The builder performance of DCAp, which was evaluated on an equal mass basis in a heavy-duty detergent formulation on standard soiled cotton cloths, is also more effective than that of DCAm.

The relatively new polycarboxylates of neutral and ionic allyl glycoside (AGlu) monomers and diacids such as maleic acid or itaconic acid were prepared by Mahrholz *et al* [84]. Three series of poly (allyl-β-D-glucofuranosiduronic acid-co-maleic acid) [p(AGlu-MA)], poly(allyl-α-D-galactopyranoside- co-maleic acid) [p(AGal-MA)] and poly(allyl-β-D-glucofuranosiduronic acid-co-itaconic acid) [p(AGlu-IA)] were obtained. The calcium sequestering capacity is in the order of p(AGlu-MA)> p(AGlu-IA)> p(AGal-MA), while their biodegradability is in the inverse order [70]. All three series have more degrees of biodegradation than poly(acrylic acid), but only p(AGlu-MA) shows better performance as a builder than poly(acrylic acid) does. p(AGlu-MA) is favored as a potentially attractive substitute of commercial copolymer of acrylic acid.

It is interesting to mention a comparative study of conventional and compact detergents performed by Sanchez Leal *et al* [85]. On the basis of the package type and the builder used, they gathered the diverse detergents in four categories: P-based conventional, P-free conventional, P-based compact, and P-free compact. The detergency (percentage of soil removal) has been determined using soiled (with carbon black/olive oil) cotton and polyester/cotton fabrics and the overall results indicate that compact STPP-built detergents show better washing performance than compositions containing zeolite-$Na_2CO_3$-polymer (6∶3∶1) ternary builder [86] and impose the lowest chemical load upon the environment for the same detergency performance except for eutrophication.

Nevertheless, the problem of replacement of STPP builder is being solved. Recently, American Agricultural Research Service scientists and Folia Inc. have developed a new, environmentally friendly co-builder from corn. They combined citric acid and sorbitol and heated them to form biodegradable polyesters. Because critic acid and sorbitol are derived mainly from cornstarch, both compounds are plentiful, renewable, and inexpensive resources. Although more new bio-based polyester is needed to obtain the same builder activity as polyacrylic acid, they have the advantage of natural degradation after use. Folia now seeks commercial-scale production capabilities of at least 1000 pounds of the bio-based polyester co-builder per hour [87]. We hope that the use of this co-builder will impose the lowest chemical load upon the environment.

## 4 PERSPECTIVES AND CONCLUSIONS

Surfactants and builders are two main ingredients in detergent formulations. There has been an emphasis over the past few years on the development of surfactants and builders with improved washing power and capacity for sequestering all the hardness, which are not only biodegradable but also non-polluting.

All major types of surfactants such as alkylbenzene sulfonates, alkyl sulfates alcohol ethoxylates, quats, and betaine have been widely used in the detergent compositions and their physicochemical behavior is relatively well understood. Because a combination surfactant system usually exhibits better detergency performance than the composition containing single-surfactant, various combination surfactant systems have been developed for detergent compositions for different uses. In addition, biodegradable surfactants such as APG and MES will be a development trend in the detergent compositions.

Many studies have been done for replacing STPP in the detergent compositions. Layered crystalline silicate ($Na_2Si_2O_5$) is a promising candidate since it combines a high performance per unit mass with a high degree of multi-functionality. Polymeric builders have good builder capacity and thus are frequently used, but most of them are not naturally biodegradable. Fortunately, a bio-based polyester co-builder, which has been made from citric acid and sorbitol, is found to be non-toxic to aquatic life and may be added to detergent in the coming years.

In future years, it will be largely driven by three factors for meeting the requirements: to improve detergency performance for various washing surfaces and oily soil removals, to reduce the price of surfactants and builders, and to derive readily biodegradable ingredients from renewable resources instead of oil reserves. The chemical industry technology will continue to move toward low-cost and highly efficient surfactants and builders for use in detergents. Detergent manufactures will strive to meet laundry, personal-care, and industrial washing demands by developing detergent compositions comprising a combination of various surfactants and builders. More and more eco-friendly, biodegradable surfactants and builders (*e.g.*, APG, MES and bio-based polyester builders) will be used in detergent compositions since they are derived mainly from inexpensive renewable resources. The use of renewable feedstocks, as compared with petroleum, will result in a reduction in the emission of fossil fuel-derived carbon dioxide, which is beneficial to the environment. On the basis of economic and environmental considerations, the commercialization of environmentally friendly surfactants and builders will increase in large amounts in detergent markets.

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