Detergents of the 21st century

Oléagineux, Corps Gras, Lipides. Volume 8, Numéro 2, 155-9, Mars - Avril 2001, Dossier : Tensioactifs : savons et détergents

Auteur(s) : Louis HO TAN TAI, Véronique NARDELLO-RATAJ, 195, avenue du Maréchal-Leclerc, 59130 Lambersart, France.

Summary : Detergents of the 21st century will depend on evolutions in household appliances, in substrates and in consumer needs. In addition, the environmental constraints, which become more and more stringent, will also play an important role, particularly in the formulations. Surfactants, which constitute one of the main raw materials in detergents, will have to be more environmentally friendly with increasing criteria of biodegradability and renewable materials. Builders (phosphates or zeolithes), heavy metal complexants (EDTA) and bleaching agents (combination perborate/TAED) are also expected to be replaced by biodegradable compounds, with better performances and lower costs. The real raw materials of the detergents of the 21st century will probably be enzymes (oxidase, hydrolase, peroxidase) which present several advantages. At the same time, efforts will be made on biodegradable packaging through the use of micro-organisms able to degrade polymers. Finally, in terms of product forms, the concept of concentration might come back through the use of tablets.

Keywords : detergent, builder, surfactant, complexant, bleaching agent, enzyme, polymer, biodegradability, environment, renewable, packaging, concentrated liquid, complete liquid.

Résumé : Les détergents du 21e siècle dépendront des évolutions dans les appareils ménagers, dans les substrats et dans les besoins des consommateurs. De plus, les contraintes environnementales, qui deviennent de plus en plus rigoureuses, joueront aussi un rôle important, en particulier dans les formulations. Les tensioactifs, qui constituent une des principales matières premières dans les détergents, devront être plus respectueux de l'environnement avec des critères croissants de biodégradabilité et de matières renouvelables. Les builders (phosphates ou zéolithes), les complexants des métaux lourds (EDTA) et les agents de blanchiment (combinaison perborate/TAED) seront aussi remplacés par des composés biodégradables, avec de meilleures performances et des prix plus bas. Les véritables matières premières des détergents du 21e siècle seront probablement les enzymes (oxydase, hydrolase, peroxydase) qui présentent plusieurs avantages. En même temps, des efforts seront faits sur les emballages biodégradables à travers l'utilisation de micro-organismes capables de dégrader les polymères. Enfin, en termes de formes de produits, le concept de concentration pourrait revenir à travers l'utilisation de tablettes.

Mots-clés : détergent, tensioactif, complexant, agent de blanchiment, enzyme, polymère, biodégradabilité, environnement, renouvelable, emballage, liquide concentré, liquide complet.

ARTICLE

It is difficult to plan, particularly for the future. When we talk about detergents of the 21st century, we must be modest and cautious. Actually, sometimes, the market does not follow the "scientific" logic, proving this is not the only factor in success. As an example, in Europe, the concept of liquid detergents for laundry was readily accepted as a product by consumers, but they were disappointed in the actual performances and the price. In the same way, concentrated powders were variously accepted among countries and even continents. Thus, if some explanations can be given in certain cases, the success or the disinterest of a product by consumers is not always straightforward to identify.

Nevertheless, some predictions have to be made. In the future, manufacturers of detergent will need to deal with constraints and pressures in numerous areas such as (i) innovations in household appliances, textiles and surfaces, (ii) environmental regulations and consumers safety issues, (iii) changes in the marketplace and (iv) changes in consumer needs.

In the present article, we will discuss the different evolutions likely to have an impact on products, the different constraints likely to influence the formulation of the products and finally, we will deal with the detergents of the 21st century.

Different evolutions

Household appliances

Several future developments, having an impact on the product itself, are expected. This particularly concerns household appliances. For fabrics washing machines, we can distinguish three types of market:

- developed countries in which almost all homes have machines (99% in France);

- Southern and Eastern Europe in which the machine market is still growing;

- the Third World in which machine ownership represents only few percents.

For dishwashers, the market is almost nonexistent in many countries. Even in countries with a high standard of living, ownership is much lower than for textile washing machines, the pace of market penetration is less important and the progression is slower.

In developed countries, the manufacturers of washing machines are trying to attract new consumers with real technological innovation and improvements, besides aesthetic improvements and lower costs. "Intelligent" machines are coming onto the market. For example, some washing machines can weigh the wash and adapt the amount of water and the duration of the cycle accordingly, or program an extra rinse cycle if there are residual traces of detergent at the end of the wash. The trend is to shorten the cycles, to reduce the amount of water used, to improve the machines generally and to increase the rinse speed.

Substrates

At the same time, substrates are all changing very quickly with, for some years, appearance of microfibers or recent return to natural fibers, in particular to cotton. In some countries such as Japan or USA, cotton now represents almost 90% of textiles sold. However, somewhat fragile colored articles continue to make up the majority of our wardrobes. Almost 4,000 different colorants are available.

In the field of dishes and other hard surfaces, the detergent industry knows a positive development. Most luxury porcelain manufacturers are now selling products that are machine washable. Other hard surfaces are becoming tougher, particularly floor coverings.

Consumer needs

Two situations exist. On one hand, in less developed countries in which formulations are more basic and more in relation to the consumer needs (in particular, in terms of cost), the main objective is more to increase volumes of products in order to enable as many people as possible to achieve at least minimal hygiene standards. On the other hand, in developed countries, consumers are more demanding in terms of:

- *Product costs.* Actually, in times of prosperity, the consumer is interested in more than simply the price of the product and may be prepared to pay a little more for a specific benefit. However, when times are harder, prices become a major criterion of choice.

- *Performance.* Wash cycle temperatures are falling and what may be enough to freshen up clothes is not enough to thoroughly clean some tenacious stains. Stain removal is the main priority and the respect of colours is another need. It is noteworthy that future products, to meet these criteria, must be both effective and not harsh. On the other hand, the fact that dosage has dropped and that, sometimes, washing is made under severe conditions (e.g. in Japan, clothes are washed in cold water short wash cycles) has to be taken into account.

- *Quality.* The physical properties of the product are very important (easy pouring, no lumps). The variation of the composition, especially for post-doses small ingredients, must be as low as possible.

- *Comfort.* The perfume must be pleasant. Consumers are spending more time at home and hence, appreciate more to be surrounded by pleasant odors, including both those on their clothes and other substrates (floors...). For hand washing products, the consumer wants milder products and good foam levels.

- *Safety.* The consumer wants more and more products that are neither harsh nor toxic.

- *Environment.* Consumers are more and more sensitive to environmental matters and are more aware of these aspects by, for example, paying attention to the chemical ingredients shown on the package.

- *Practicality.* A certain contradiction exists. Actually, consumers want both to simplify household tasks in, for example, multifunctional products (e.g. detergent with softeners or 2-in-1 shampoos) and to have perfect results which may lead to the development of a multiplicity of specialized products.

- *Hygiene.* We know that some bacteria can become resistant to antibiotics. There are some food poisoning on account of dishes which have not been washed properly. Aware of these problems, consumers are increasingly demanding antibacterial products for both clothes washing (especially at low temperature) and hard surface cleaning.

Various environmental and regulatory constraints

Environmental constraints

Respect for the environment can be summariz-ed by the following sentence from the Bruntland Commission report in 1987: "The objective is to satisfy present needs without scarifying those of future generation". As responsible detergent manufacturers, it is our duty to contribute to respect for the environment in the following areas:

- *Water.* While in developed countries, we can consume as much water as we like, most of the world's population does not have enough water for domestic use and sometimes does not even have clean drinking water. It is essential to do everything we can to save water in our production plants (using recycled water for example) and through the products that we develop in order to wash and to clean with less water.

- *Energy.* We must consider energy reduction on different ways: by developing products for low temperature washing and by promoting and developing production processes that consume less energy.

- *Natural resources.* Fewer raw materials and packaging materials should be consumed and the use of renewable raw materials should be encouraged.

- *Pollution.* We must be aware of pollution by factories and consumers in terms of air quality and waste poured into rivers or soils.

Life-cycle analysis will be necessary and systematic for all modifications.

Regulations and associations

In the future, it is unlikely that legislative bodies will be solely responsible for the control of the environmental problems. There are actually more and more voluntary agreements between government and certain companies (*via* their associations). Whatever happens, the debate should be scientific and not emotional. Acting in this manner could have avoided the unfortunate conflict in Denmark with regards to restrictions on the use of Linear Alkylbenzene Sulfonates (LAS). Actually, under pressure from farmers who use sludge from water treatment plants, the government arbitrarily fixed the authorized level of LAS (decree n° 832) without consulting the detergent industry or consider-ing any scientific evidence. Another example is the problem of phosphates for which the position of experts is not unanimous. Beyond the exploitation media few years ago, it is advisable to adopt a rigorous approach that analyses all the terms of the equation and to get on to the question

with serenity in order to avoid impulsive reactions. On the other hand, the wish for opening, by both government and industry, will allow to provide exact and reliable data, supported by experts when necessary, that will be beyond question by certain pressure groups. For detergent manufacturers, it is required:

- to maintain a dialogue with the authorities and associations (e.g. AISD in France, AISE in Europe, SDA in the USA);

- to operate transparently by giving the relevant authorities open access to all of the required and relevant scientific facts at their disposal;

- to communicate their know-how and their state of knowledge of the environment and to explain their environmental policy;

- to educate consumers in better ways to use their products;

- to avoid "eco-marketing" which would damage the image of the entire industry.

The challenge for manufacturers

A product development is a long process even if implemented resources are huge (more than 1,000 patents between 1970 and 1994). However, today, evolution is so rapid that innovation has to move just as quickly. Innovation must therefore move even faster!

Research and development

Challenge requires considerable investment and the costs are impressive. A large multinational business in the consumer goods business spent more than US $ 800 million on research and development in 1995. It is not unusual for such companies to spend between 3 and 8% of their turn over on research and development. It is noteworthy that 90% of all research and development funds are expended in five countries (United States, Germany, Japan, Great Britain and France) even though these countries represent only 10% of the world's markets. This may be understandable because in industrialized countries, products are much more sophisticat-ed than in developing countries and therefore, there are more research and development facilities. In addition, the results of this research can be transferred very quickly and easily, at least by multinational companies, from one country to another.

Finally, the question of globalization, regionalization and localization has to be considered. The general policy of multinational businesses is to concentrate on their core businesses and to sell any nonessential businesses in order to invest more important markets (e.g. China, India or Latin America). In such cases, the transfer technology is relatively easy but it is often detrimental to local businesses. On the other hand, some regional companies are sufficiently strong in research and development so that they do not suffer from the effects of globalization. They are able to survive and prosper in their own field. This is the case of Japanese companies. Finally, with their limited resources, local companies cannot afford significant expenditures in research and development. They have to rely on unpatented conventional technology, which over time can be a disadvantage.

Partnerships

Some partnerships have to be developed with:

- *Official bodies and various associations.* These require honesty, open-mindedness and confidence based on scientific facts.

- *Manufacturers of laundry appliances.* Changes in washing machines can come about only if there is close cooperation between machine and detergent manufacturers. The ideal situation would be for the latter to be involved in washing machine design in order to avoid any risk of incompatibility between machine and product.

- *Manufacturers of substrates.* In a same manner, manufacturers of products must keep themselves informed of the technical evolutions in the area of substrates (textiles, dishware, hard surfaces).

- *Raw material suppliers.* Until now, manufacturers relied on their own basic laboratories for the discovery of new molecules and development of processes for their synthesis. Then, the manufacturer detergent would approach suppliers to negotiate production and costs for the new materials. At the same time, raw material manufacturers also work to discover new compounds that they try to sell to their customers. There was few collaboration and cooperation. Each party safeguards its research programs, the initial results, right up to the final stages. However, today, in order to accelerate innovation and to avoid wasting resources, a different mentality is required, involving closer collaboration and partnerships contracts between customers and suppliers. This new trend would seem more logical and more efficient. Actually, the development of new molecules is becoming more complex and also more expensive. In addition, all companies are trying to reduce their indirect costs which have significant consequences for research and development.

We dare to hope that this new approach in terms of partnerships will be the key to innovation in the 21st century.

The detergents of the 21st century [1]

This part will deal with raw materials, packaging and product forms.

Raw materials

Surfactants [2-5]

Today, manufacturers have to develop more environmentally friendly surfactants that increasingly meet criteria of biodegradability and come from renewable raw materials.

* *LAS: linear alkyl sulfonate*

ABS (AlkylBenzene Sulfonate) is the most widely used surfactant. It can be branched but in that case, it presents a very slow rate of breakdown by microorganisms. On the other hand, when it is linear, it is called LAS (Linear AlkylBenzene Sulfonate) and has an increased biodegradability. LAS has not yet completely replaced ABS but it will certainly be used for many years to come *(Figure 1)*.

* *PAS: primary alcohol sulfate*

They are more biodegradable (and can be renewable raw materials) which are slowly gaining ground. In certain coconut-rich countries, PAS has already overtaken LAS. In the Philippines, for example, manufacturers are obliged by law to use 60% PAS in their active systems. PAS will probably gradually completely replace LAS.

$R\text{-}O\text{-}SO_3H$

* *Nonionics*

The most widely used nonionic surfactants are still ethoxylated fatty alcohols. In time, fatty alcohols will come from renewable sources (vegetables) and ethoxylated alcohols with a narrower ethylene oxide distribution will be used.

* *New molecules*

Alkylpolyglucosides (APG) *(Figure 2a)* *N*-methyl glucosamide *(Figure 2b)* or methyl ester sulfonates (MES) *(Figure 2c)* are easily synthesized, biodegradable and renewable raw materials which perform well. However, they are still more expensive than LAS or PAS. Nevertheless, they are certainly molecules of the near future, as their prices drop with increasing volumes.

* *Cationics*

Quaternary esters are already being used and will be still more widely used in the near future. The pathway of their degradation (hydrolysis) is known and their efficacy has been proven. Other molecules under development will be soon available in the fabric softener area. For example, we can mention tertiary amidoamines, quaternary dialkylamidoamines and dialkylimidazoline esters *(Figure 3)*.

* *Molecules containing one or several nitrogen atoms*

They will be used less frequently because of the potential problem posed by the formation of nitrosamines.

Builders *[6-8]*

Originally, the term "builders" denoted additives that were combined with soap to improve wash performance. Then, it was used to describe water softeners, particularly phosphates and subsequently zeolites, silicates or carbonates.

* *Phosphates*

Since the Second World War, detergent formulations have included phosphates, mainly tripolyphosphates. However, in developed countries, the use of phosphates has decreased steadily (presently about 20% instead of about 40% several years ago) for cost reasons and more importantly for environmental reasons. Nevertheless, it will now remain stable for some time until an "ideal" builder has been found. They have been replaced by ecologically more acceptable zeolites which

require the presence of polycarboxylate cobuilder. In developing countries, phosphates will be used for several decades to come because of their multifunctional performances and their cost. They will also be true in countries in which water is soft and there are no eutrophication problems.

* *Zeolites*

Zeolites, which are insoluble raw materials, are sodium aluminosilicates, $Na_{12}(AlO_2)_{12}(SiO_2)_{12}. 27H_2O$. For environmental reasons, the use of ion exchangers has increased considerably over the past few years. A period of stability or even reduction in consumption is likely. Actually, after a reflection time, some experts are beginning to question this raw material as a phosphate substitute. Suppliers and manufacturers are probably working hard to find an "ideal" builder that performs well, is biodegradable and not expensive.

* *Layered silicates*

These raw materials are soluble builders. They are already being used in some detergent products. We hope that others will become available in the near future, and will develop significantly in years ahead.

Heavy metal complexants

The search for new complexing agents is not straightforward. More biodegradable molecules will take over products such as the rapidly disappearing EDTA. Such new molecules are, for example, sodium methylglycinediacetate (MGDA) and sodium ethylenediamine mono- and disuccinate (EDMS and EDDS). EDMS has been presented by Dow Chemical as a biodegradable molecule, with very good complexing properties with Fe^{3+} and Ca^{2+} ions. EDDS is also biodegradable but is more expensive *(Figure 4).*

Bleaching agents *[9]*

The perborate/TAED (tetraacetylethylenediamine) combination still has a good future as the basic system for laundry and for automatic dishwashing detergents. However, pressures may build up against the levels of boron in drinking water, in which case the use of percarbonate could develop strongly. On the other hand, in the decades ahead, the trend toward lower wash temperatures will require more effective ingredients such as biodegradable activators. They would be catalysts for dishwashing or laundering, provided the new molecules do not damage the wash, as well as other peracids, for example phtalimidoperoxycaproic acid (PAP). New molecules in this field are expected *(Figure 5)*.

Polymers *[10, 11]*

Today, acrylic homopolymers and acrylic/maleic copolymers are widely used but they will progressively be replaced by biodegradable and renewable materials. Polymers used as cobuilders will reduce the levels of builders or complexing agents used in formulations. Their use will grow but the problem of their biodegradability will require to be a subject of further research. Two promising copolymers can be pointed out: polyacetals and poly-L-aspartic acid *(Figure 6)*.

Other polymers will also be developed with soil release, dye transfer inhibition and antiredeposition functionality. On the other hand, the current use of polycarboxylates and acrylic/maleic acid copolymers will continue in a medium term.

Enzymes *[12, 13]*

For the following reasons, enzymes are probably the real ingredients of the future:

- they are effective at low incorporation levels, which is significant for concentrated products;

- they are the "ideal" raw material for the respect of the environment;

- they can be handled without risk.

Moreover, biotechnology research is trying to "manufacture" enzyme types with the precise performance features required, such as enzymes effective in specific stains. We can mention oxidase, hydrolase, peroxidase and pectinase, as well as enzymes that work under difficult conditions of low temperature, high or low pH, shorter action times, or lower surfactant levels. Such enzymes have not yet been used in detergent formulations and should reach the market in the years ahead, particularly for bleaching.

Fluorescent whitening agents

Whiteness and brightness will still be consumer demand and fluorescent whitening agents will still be present in detergent formulations. In that field, new molecules will have to be biodegradable.

Perfumes

The detergent industry uses more perfume than any other industry in the world. The need will remain for perfumes that are pleasant, and signal cleanness and efficacy. Sophistication will increase in the years ahead with a move toward luxury perfumery notes. Developments will also take place in terms of safety and respect for the environment. Levels of other non biodegradable molecules will have to be reduced. Today, polycyclic musks are being questioned strongly with regard to their lack of biodegradability and poor solubility. Replacements for these important fragrance constituents, which provide lasting perfume on fabrics, are being studied by the perfumery industry and represent a major challenge for perfumers.

Solvents

Solvents that are unsafe or that present a risk for the environment no longer will be used and less noxious solvents, such as short alkyl chain amphiphile molecules or essential oils will be adopted.

Packaging

Today, in addition to its protective function, packaging must fight for the consumer's attention and must be as functional as possible, with still environmental considerations, which require that packaging material not be excessive, recyclable and safely disposable. The trend is to reduce packaging resulting in the concentration of products, with a particular emphasis on the aesthetic and functional aspects.

In the future, efforts will be made on biodegradable packaging. Some micro-organisms are able to degrade polymers and this technique seems to be attracting some interest. There are already applications, such as McDonald's in Austria, which uses corn-based polymer knives and forks that biodegrade in a few months, Yogurt containers based on polylactic acid (APL) in Germany. APL is obtained by fermentation of dextrose into lactic acid which is then polymerized. Today, the cost of tomorrow's materials is still very high (from 2 to 10 times more expensive than the corresponding plastic) but it is good to bet that, in a few years, with evolution of the techniques, such materials will be readily present in our supermarkets.

Product forms

In the short-to-medium term, laundry detergents should evolve toward greater concentration and complete liquids. Concentrated powders have not met the anticipated level of success and a return to conventional powders has appeared in Europe. If this trend continues, there would be a step backward and the concentration concept will have to be used in other forms. A compromise solution between the existing concentrated and conventional powders would have to be found. One of them would be to remove everything from the formulation that is not functional such as water or sodium sulfate (more than 20% in some cases). On the other hand, the idea of concentration could be applied to other forms than liquids. For example, tablets for laundering have already made their appearance in Spain, France and Great-Britain. This concept is maybe one of the solutions for the future, if tablets will meet with the same level of success as they have in machine dishwashing (more than 50% of the market). Complete liquids, with bleaching agents, should totally satisfy some users. Finally, in the machine dishwashing area, pre-dosed products will continue to progress and new developments will move toward greater simplification. In personal care, product form probably will not change significantly but the product will become more sophisticated and provide better skin care. Hard surface cleaning will not be revolutionized but there may be greater specialization by type of surface to be cleaned.

CONCLUSION

Because of their advertising (particularly on television), consumer products including detergents may have a poor brand image at least amongst certain segments of the population. Through this article, we aim to show the extent of the Research and Development and industrial equipment resources that are put behind the products concerned to support the efforts by the main manufacturers to produce household detergents. It is firstly to satisfy consumer needs, to meet these needs with quality products, which are efficient, safe to use and without danger for our environment.

Our mission is also to allow as many people as possible to have access to a decent level of hygiene, and it is certain that we, the detergents manufacturers, have a role to play in the health of populations in under developed countries. Doctor V.W. Greene, professor of environmental health and microbiology at the University of Minnesota, showed clearly in "Cleanliness and the Health Revolution - New York 1983" (a study conducted in more than 120 countries) that there is a direct relationship between soap and detergent consumption in a country and its rate of infant mortality.

In Afghanistan where baths were forbidden by religion, the population consumed 0.6 kg of soap per inhabitant in 1978, and the rate of infant mortality was 18%. By comparison, we should underline that the rate of infant mortality in developed countries is less than 2%, and the consumption of soaps and detergents is generally more than 10 or even 20 kg per inhabitant per year.

REFERENCES

1. LE HEN FERRENBACH C, BRACKMANN B, HÖVELMANN P (1996). Tendances dans les détergents et les produits d'hygiène corporelle. *L'Actualité chimique*, 2-3: 82-90.

2. ROSEN MJ (1978). *Surfactants and Interfacial Phenomena.* New York: John Wiley and sons: 94-162.

3. LINFIELD WM (1976). *Anionic Surfactants*. *Surfactant Science*, vol. 7, Part 1. New York: Marcel Dekker Inc.

4. SCHINK M (1967). *Nonionic Surfactants. Surfactant Science*, vol. 1. New York: Marcel Dekker Inc.

5. FALBE JU (1987). *Surfactants in consumer products.* Berlin: Springer-Verlag.

6. Unilever (1991). EP Patent 0 414 285.

7. TOMLINSON AGG (1998). Modern geolithes: structure and function in detergents and petrochemicals. *Material Science Foundations,* vol. 3.

8. HEINZMAN S (1998). Small molecule polycarboxylate Builders. *Journal of Surfactants and Detergents,* 1, AOCS Press: 105-8.

9. Lever Brothers (1992). US Patent 5 160 655.

10. Colgate-Palmolive (1997). US Patent 5 602 092.

11. BERTLEFF W, NEUMANN P, BAUR R, KIESSLING D (1998). Aspects of polymer use in detergents. *J Surfactants Detergents*, 1, AOCS Press: 419-24.

12. OLSEN HS, FALHOT P (1998). The role of enzymes in modern detergency. *J Surfactants Detergents,* 1, AOCS Press: 555-67.

13. OTHMER K (1994). *Enzyme applications,* vol. 9. *Encycl Chem Tech* 4^{e} edition: 558-96.

Illustrations

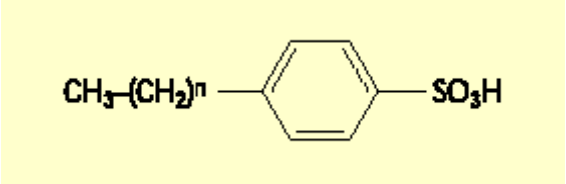

Figure 1. *Linear ABS (LAS).*

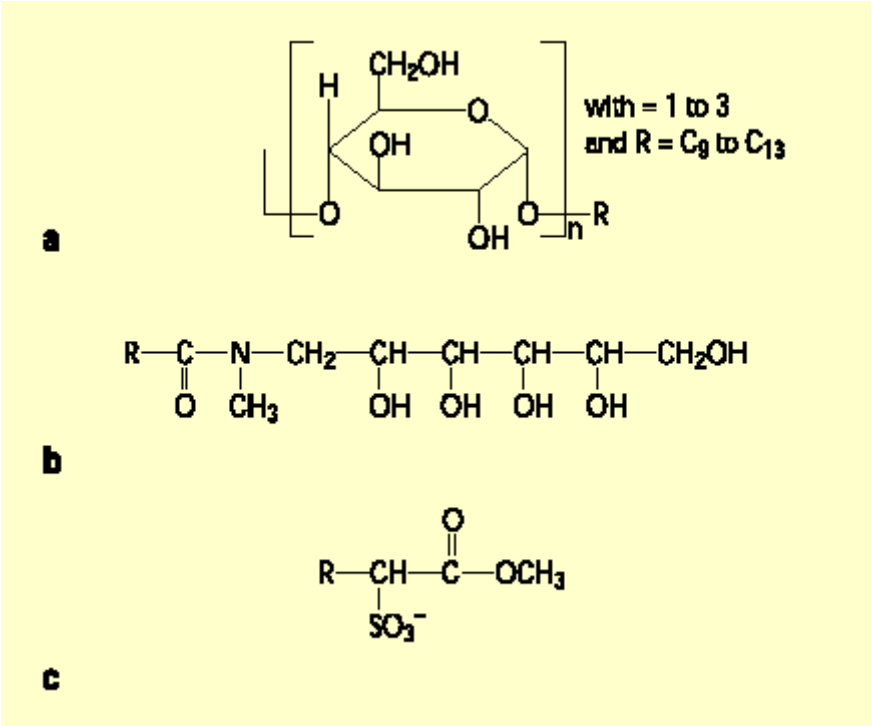

Figure 2. *a: APG. b:* N-*methylglucosamide. c: MES.*

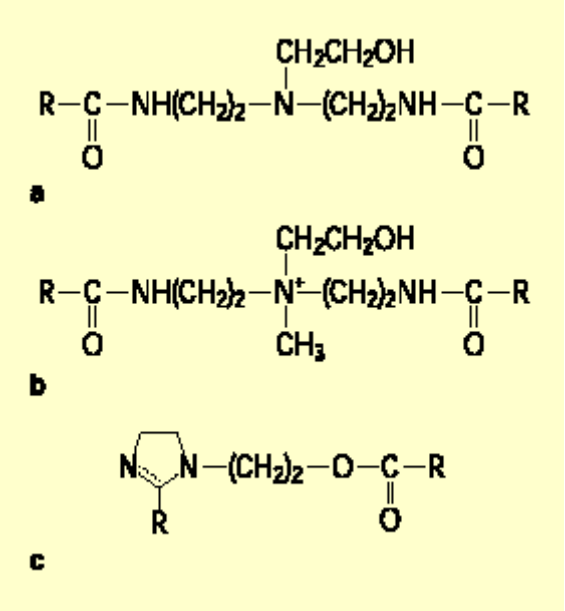

Figure 3. *a: Tertiary amidoamine. b: Quaternary dialkylamidoamine. c: Dialkylimidazoline ester.*

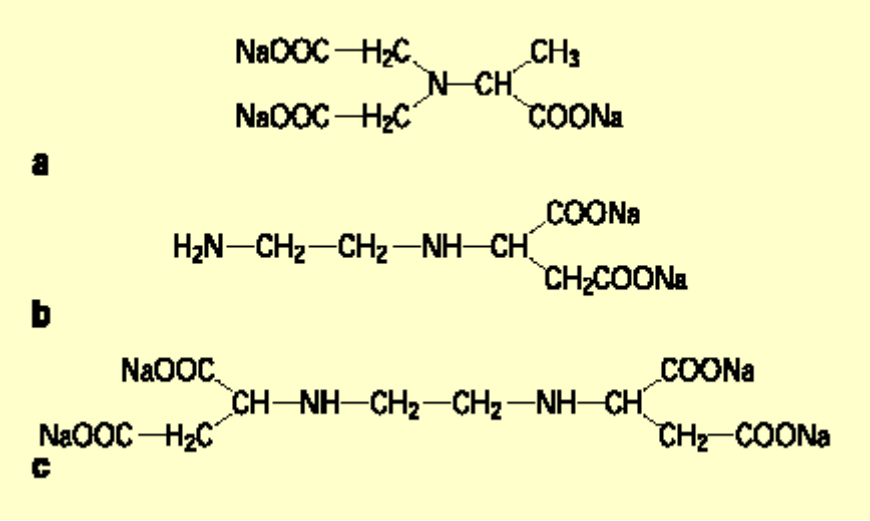

Figure 4. *a: MGDA. b: EDMS. c: EDDS.*

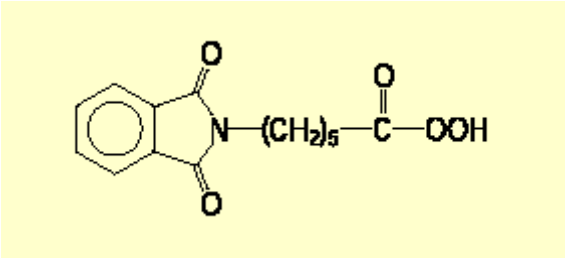

Figure 5. *Phtalimidoperoxycaproic acid (PAP).*

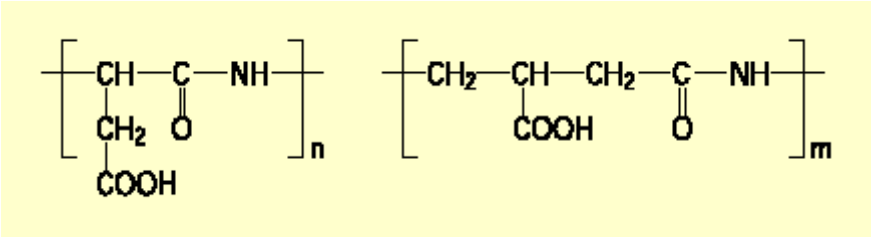

Figure 6. *Poly-L-aspartic acid.*