

## Industrial development and application of biobased oleochemicals\*

Karlheinz Hill

*Cognis GmbH, Monheim, Germany*

**Abstract:** In concepts for new products, performance, product safety, and product economy criteria are equally important. They are taken into account already when the raw materials base for a new industrial product development is defined. Here, renewable resources gain—again after the earlier “green trend” in the 1980s—increasing attention as an alternative raw materials source compared to fossil feedstock. The industrial use of carbohydrates, proteins, and vegetable oils aligns perfectly with the principles of Responsible Care and is an important part of green chemistry and sustainability in general.

Since the 1950s, oleochemistry has grown to a major research and technology area in several institutions and industries. A large variety of products based on fats and oils have been developed since then for different uses, such as specialties for polymer applications, biodegradable mineral oil replacements for lubricants, and surfactants and emulsifiers for the home and personal-care industries. However, at present it seems that the use of renewable resources, especially vegetable oils, has to compete more and more with the increasing demand for bioenergy, which could cause an unbalanced supply and demand in the future or even a threat for the increasing demand for food in certain areas of the world.

**Keywords:** carbohydrates; emollients; emulsifiers; lubricants; oleochemicals; polymers; surfactants.

### RAW MATERIALS SITUATION [1–4]

Carbohydrates—in particular, starch, cellulose, and sucrose—proteins and natural fats and oils are key raw materials for the chemical industry using renewable resources. Although biomass in general is available in large amounts (e.g., cellulose), the annual production volumes of selected commodities are still small compared to coal or crude oil (Table 1). So far, the volumes were adjusted according to the different demands. In particular, in the case of natural oils and fats, the production volume steadily increased from 30 million tons in 1960 to 131 million tons in 2004 [1]. Most of it is used for food, a minor amount for animal feed and chemistry (Fig. 1) [2]. Until now, availabilities and the different applications were quite balanced.

However, for some time we have observed a shift toward an increasing use of natural vegetable oils for bioenergy and biofuels, with an expected share of 15 % in 2012. This increase originally started in Europe years ago with the development of biodiesel from rapeseed, to be followed later on with further development based on other vegetable oils, such as palm and soybean. This is one consequence of political measures such as the European Biofuel Directive 2003/30/EC, which requires a minimum proportion of biofuel in the market to comply with the Kyoto Protocol. Biodiesel production volumes were expanded significantly in the recent past, and this trend is expected to continue in Europe and other re-

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gions such as South East Asia, South America, and India, with a further increase in production capacities forecasted at least for the next 10 years (Fig. 1) [4a]. After that, it might slow down again, when the so-called second-generation products, such as sundiesel or biomass-to-liquid fuels, will be ready to be launched to the market [4b]. Those technologies are definitely needed as it can be assumed that even with increasing production volumes for fats and oils, the future bioenergy and biofuel demand cannot be satisfied by this source by far [4]. In the meantime, however, the high demands for biodiesel, further stimulated by subsidies, could create not only an over-supply of glycerol [1c], but also a strong competition with the established uses for vegetable oils such as nutrition and chemical industry (oleochemistry).

**Table 1** Annual production of commodities worldwide (2004, million tons).<sup>a</sup>

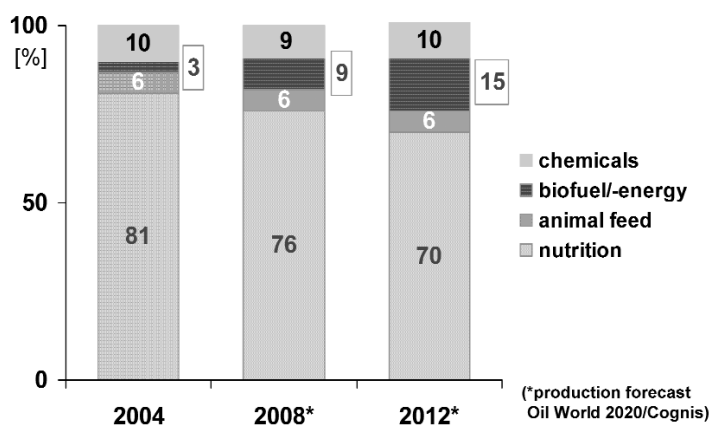
Wheat	Rice	Starch	Sugar <sup>b</sup>	Fats and oils <sup>c</sup>	Crude oil	Coal <sup>d</sup>
610	610	40	145	131	3600	3800

<sup>a</sup>Sources: OilWorld, USDA, Industrierverband Agrar, Wikipedia.

<sup>b</sup>From beets and cane.

<sup>c</sup>Vegetable- and animal-based, thereof 13 million tons for industrial use (incl. soap production).

<sup>d</sup>As SKE (1 kg SKE = 0.984 kg bituminous coal = 29.307.6 kJ).



**Fig. 1** World production of oils and fats and uses in 2004, 2008 (estimated), and 2012 (estimated) with increasing new demand elements biofuel and bioenergy (relative shares in %) (source: Oil World/Cognis).

## ECOLOGICAL COMPATIBILITY

Many efforts to define “green” and “sustainable” have been undertaken, and principles for green chemistry have been defined [5a]. Metrics have been developed and also applied, for example, assessing environmental, health, and safety hazards, including life-cycle inventories (“cradle to factory”) and life-cycle assessments (“cradle to grave”) [5b,c]. Based on results from life-cycle assessments and ecological and toxicological studies for selected cases, one can assume that products based on renewable resources usually are more ecologically compatible when compared with petrochemical-based substances—an important criterion in the development of a new product, just as price and performance are [5d–f]. However, this general assumption has to be proven for each new product again. Therefore, ecological compatibility plays a decisive role in all research and development projects. Basically, it covers two different aspects: remaining in the environment and the effects on the environment (Table 2). Various criteria are used to evaluate these two aspects. By exposure analysis, the expected environ-

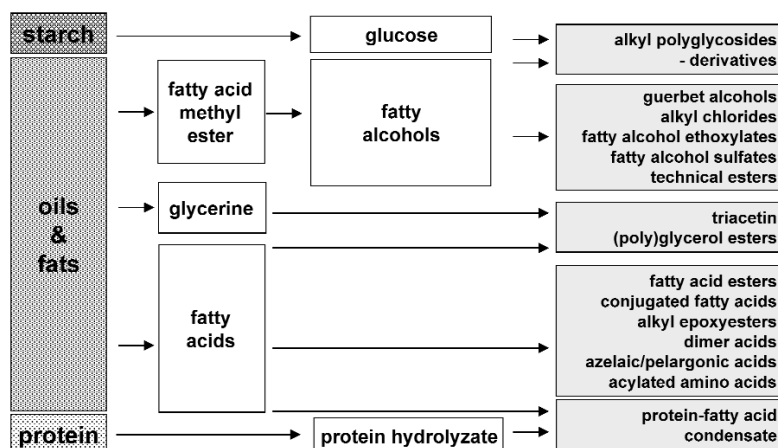
mental concentration of a particular substance (in waste water, in exhaust gases, or in a sewage treatment plant) is estimated, taking into consideration the amount of the substance produced and its biodegradation behavior. The effect on the environment (e.g., toxicity to organisms such as fish, algae, or microorganisms) is determined by a series of standardized testing methods. The two results are compared with each other. If the expected environmental concentration of a particular substance is less than the amount at which negative effects can no longer be determined, then the product is ecologically compatible [6]. Apart from the ecological investigations, toxicological tests and microbiological and dermatological investigations are also carried out. In the framework of a successful marketing strategy, all parameters, which are relevant to product safety for environment and consumer, are evaluated at each product development stage (selection of raw materials, development of test formulations and application tests, process development, development of packaging, testing consumer satisfaction in test markets).

**Table 2** Evaluation of environmental compatibility of chemicals.

	Method	Result
Basic information		
– Environmental fate	Biodegradation tests	
– Environmental effect	Ecotoxicity tests	
Criteria		
– Environmental concentration	Exposure analysis	PEC: Predicted environmental concentration
– Ecotoxicological concentration	Biodegradation	PNEC: Predicted no effect concentration
<b>Evaluation</b>	<b>PEC vs. PNEC</b>	<b>PEC &lt; PNEC: environmentally compatible</b>

## EXAMPLES OF PRODUCTS

Oils and fats are triglycerides with different composition of the alkyl chains depending on their origin. In industrial processing, they are transferred into fatty acid methyl esters, fatty acids, glycerol, and, as hydrogenation products of the fatty acid methyl esters, fatty alcohols by applying standard manufacturing technologies. Further chemical processes lead to the desired specialty chemicals (Scheme 1) [1,2].



**Scheme 1** Industrial processing of natural oils and fats and selected product derivatives.

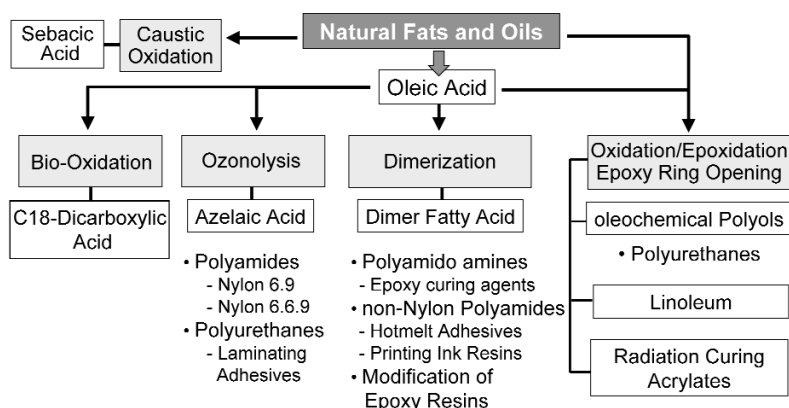
## Oleochemicals for polymer applications [7–9]

Oleochemicals as polymer materials represent a relatively small market, but are well established. We have to keep in mind that before crude oil was explored the only possibility to do chemistry was by using renewable resources. One example is linseed oil, which is used to produce linoleum. Here, the demand has increased from 10 000 tons in 1975 to 50 000 tons in 1998 (coming from 120 000 tons in 1960!) [8a]. Another example: epoxidized soybean oil (ESO) as a plastic and coating additive, has a relatively stable market of approximately 100 000 tons/year [8b]. Table 3 summarizes major products and uses according to ref. [7]. It is worth mentioning that the dicarboxylic acids are industrially produced either via ozonolysis of oleic acid to produce azelaic acid (one of the few examples of large-scale industrial ozonolysis) or by dimerization of linoleic and oleic acid to obtain complex mixtures of high-molecular-weight diacids (e.g., EMPOL<sup>®</sup> types), originally introduced in the 1950s by General Mills Chemicals and Emery (both now Cognis Corp.). Scheme 2 lays out the most-used manufacturing pathways [2c]. In a variety of polymer applications, such as coatings, large amount of solvents have to be used, including hydrocarbon and chlorinated solvents. Here, a clear trend is seen toward the so-called “green solvents”, such as ester solvents, typically produced from naturally based fatty acids and/or fatty alcohols, representing the largest group [1c].

**Table 3** Oleochemicals for polymers: selected examples [7].

	Product/use	Natural source
<b>Polymer materials</b>		
– polymerized soybean oil, castor oil	drying oils	soybean oil, castor oil
– polymerized linseed oil	linoleum	linseed oil
<b>Polymer additives</b>		
– epoxides	stabilizers, plasticizers	soybean oil
– soaps (Ba/Cd, Ca/Zn)	stabilizers	stearic acid
– fatty acid esters, amides	lubricants	rapeseed oil
<b>Building blocks for polymers</b>		
– dicarboxylic acids	polyamides, polyesters,	tall oil, soybean oil, castor
– ether-/ester polyols	alkyd resins, polyurethanes	oil, sunflower oil, linseed oil
<b>Natural fiber-reinforced composites<sup>a</sup></b>		
– epoxides	monomers for	soybean oil, sunflower oil
– maleates	polymeric	
– amides	matrices	

<sup>a</sup>Under development according to refs. [2c,8].

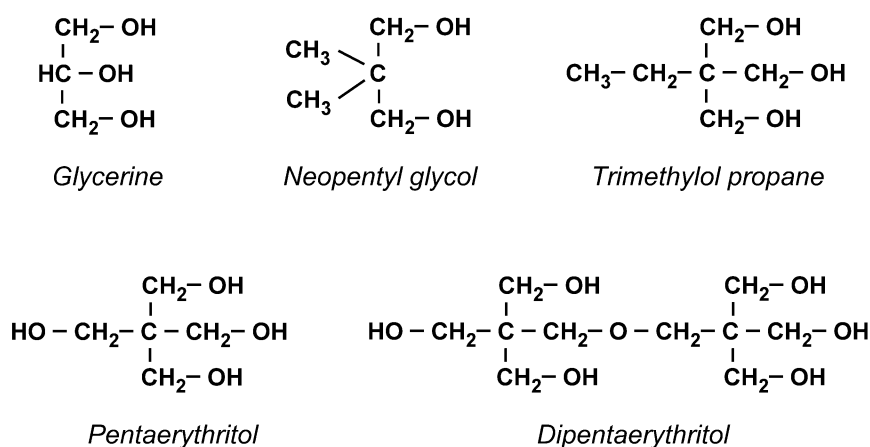


**Scheme 2** Building blocks for polymers based on natural oils from ref. [2c].

### Biodegradable fatty acid esters for lubricants [10]

Apart from being used as “biodiesel”, fatty acid esters, which are obtained from fatty acids and alcohols, are becoming increasingly interesting as biodegradable replacements for mineral oils. In some application areas such as chain saw oil, gearbox oils, hydraulic oils, and lubricants for off-shore crude oil exploration, certain oleochemical products have already proved themselves and are well established.

Esters for lubricant applications are divided into five groups: monocarboxylic acid esters (mono-esters), dicarboxylic acid esters (diesters), glycerol esters, polyol esters, and complex esters. Different types of alcohols (Fig. 2) are combined with mono- or diacids (dimer fatty acids). Although the diesters already possess an excellent lubricating effect, their thermal stability is surpassed by the polyol esters. Complex esters are formed by esterification of polyols with mixtures of mono-, di-, and tricarboxylic acids and are oligomeric mixtures, which, from a technical application viewpoint, are characterized by their high shear stability [10a].



**Fig. 2** Polyols used for the manufacturing of complex esters.

The European potential market for lubricants was estimated in the late 1990s to be 500 000–1 000 000 tons/year [10b,c]. Table 4 summarizes the major applications.

**Table 4** Global potential market of biodegradable lubricants (1000 tons/year).<sup>a</sup>

Application	Total	Biodegradable lubricants
Automotive oils	2305	250 <sup>b</sup>
Hydraulic oils	750	200
Turbine oils	200	20
Compressor oils	65	25
Industrial gear oils	200	10
Metal working oils	500	10
Demolding oils	110	110
Chainsaw oils	60	60
Process oils	600	200
Lubricating greases	100	100

<sup>a</sup>According to ref. [10b].

<sup>b</sup>Including synthetic lubricants (210).

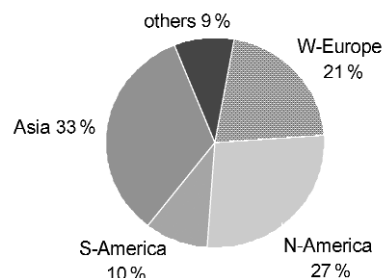
The decisive fact is that the specially designed fatty acid esters which are used as replacements for mineral oil products not only have ecologically compatible properties, but also a comparable or even better performance. In fact, this could be clearly shown when using esters as lubricants in crude oil exploration. In coastal drillings (e.g., in the North Sea), the demands are particularly high: the drilling fluid is pumped to the surface together with the drill cuttings and after coarse separation disposed of directly into the sea. Apart from the good lubricating effect, the biodegradability assumes a particular importance in this application. A specially developed fatty acid ester (e.g., **RADIAGREEN<sup>®</sup>**, **Petrofree<sup>®</sup>**) fulfils not only the requirements regarding biodegradability, but also has a better lubricating effect when compared with products based on mineral oils [11].

### Surfactants and emulsifiers derived from vegetable oil-based fatty alcohols and fatty acids [12]

Surfactants are used in a wide range of fields. By far, the most important field of application is the washing and cleansing sector as well as textile treatment and cosmetics; these use more than 50 % of the total amount of surfactants. Surfactants are also used in the food sector, in crop protection, mining, and the production of paints, coatings, inks, and adhesives. The basic manufacturing routes to important surfactants are laid out in Scheme 3 [2c]. It is true that the most important surfactant from the amount produced apart from soap is still the petrochemical-based alkyl benzene sulfonate; however, in recent years a continuous trend toward surfactants based on renewable resources has become apparent [12a]. The total worldwide market amounts to approximately 19 million tons (2000, incl. soap). The amounts involved, broken down into the individual surfactant classes and regional share, are summarized in Table 5 [12b].

**Table 5** Global surfactant consumption in 2000 (volumes in 1000 tons; shares in %).

Surfactant class	Volume <sup>a</sup>	Regional share (%) <sup>b</sup>
<b>Soap</b>	8800	
<b>Anionic surfactants</b>		
– alkyl benzene sulfonates	3400	
– fatty alcohol ether sulfates	1000	
– fatty alcohol sulfates	500	
<b>Nonionic surfactants</b>		
– alcohol ethoxylates	800	
– alkylphenol ethoxylates	700	
<b>Cationic surfactants</b>	810	
<b>Amphoteric surfactants</b>	180	
<b>Others</b> (incl. carbohydrate-based surfactants)	2900	

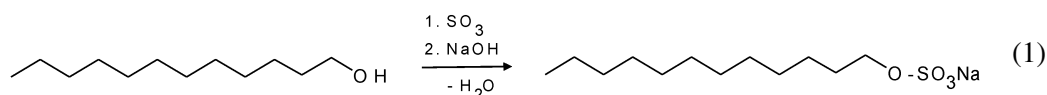


<sup>a</sup>*Soap, Perf., Cosm.*, November 2000, p. 51; Colin A. Houston & Associates, Inc.

<sup>b</sup>According to ref. [12b].

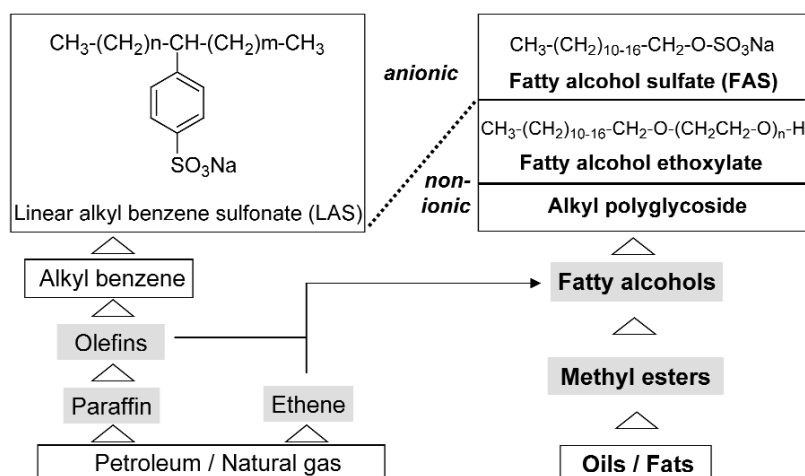
#### Fatty alcohol sulfate

Fatty alcohol sulfate (FAS) has been known for a long time and is used as surfactant in various products, for example, in detergents. It is produced from fatty alcohol by reaction with sulfur trioxide (SO<sub>3</sub>) gas, typically in a falling-film reactor. The crude product is then neutralized with aqueous sodium hydroxide (eq. 1). Certain product forms, such as aqueous solutions or granulates, are typically produced according to the requirements from the market. FASs are readily biodegradable (no metabolites in the degradation) under both aerobic and anaerobic conditions.



Since FASs can be produced either from vegetable oil- or petrochemical-based fatty alcohol (Scheme 3), both types have been evaluated in a life-cycle analysis with a positive overall result for the natural-based product [5d,e]. In the case of the vegetable-based FAS, the analysis starts with the harvesting of the oil fruits (palm kernels or coconuts) and their processing to isolate the desired plant oil. Subsequent transesterification and hydrogenation of the methyl ester intermediates lead to the fatty alcohols, which are finally sulfated to produce the desired product. Based on this analysis, the environmental impact of vegetable oil-based FAS compared to the petrochemical-based product is as follows:

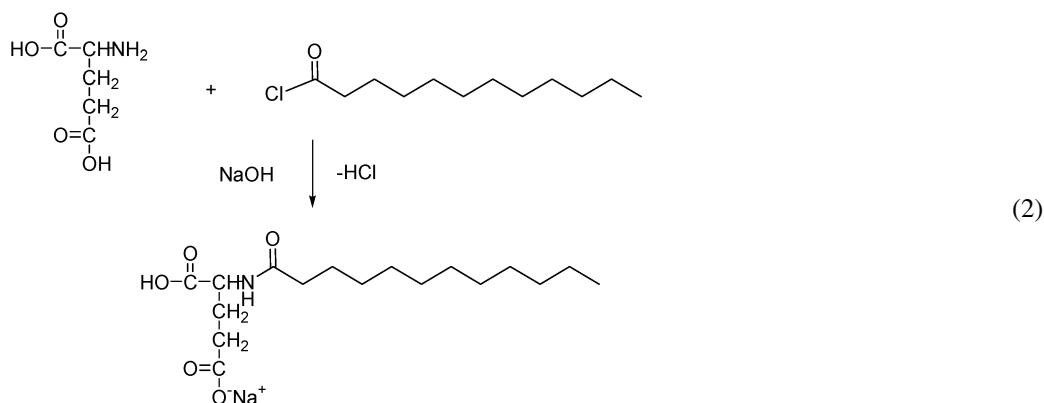
- 70 % less use of fossil resources
- 50 % less emissions to the atmosphere
- 15 % less waste
- 50 % more emission to water (low toxic waste water from small, decentralized oil plants)



**Scheme 3** Production of surfactants and examples of products from ref. [2c].

### *Acylated proteins and amino acids (protein-fatty acid condensates) [13]*

Protein-fatty acid condensates consist of fatty acids (from vegetable oil) and proteins, which can be obtained from both animal source (e.g., leather waste) and—especially when used for cosmetic products—from many plants, such as wheat, rice, soybean, with the protein part representing the hydrophilic moiety in the surfactant structure. The products are obtained industrially by applying the well-known “Schotten–Baumann” conditions (eq. 2). Instead of the proteins, pure amino acids, such as glutamic acid, are used as well in the manufacture of the corresponding acylated products industrially (e.g., Ajinomoto, Cognis). Both types are known for an excellent skin compatibility and a good body and skin cleansing effect. Synergistic effects are described if combined with other surfactants, where even small additions of the acylated protein hydrolyzate improve the skin compatibility significantly [13]. In the personal-care market, fatty acid derivatives of proteins and amino acids are mainly used in mild shower and bath products, mild shampoos, surfactant-based face cleansers, cold-wave preparations and fixatives, baby wash formulations, as well as special emulsifiers for leave-on products.

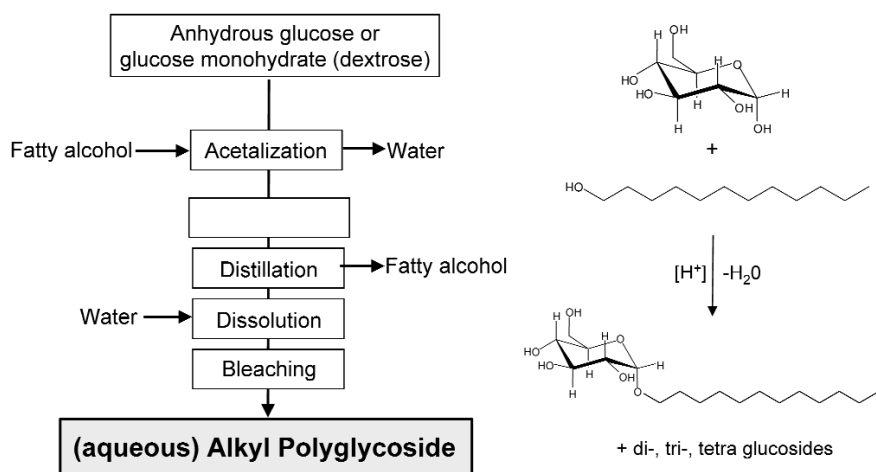


**Carbohydrate-based surfactants: Alkyl polyglycosides [14]**

Other than proteins, carbohydrates are also able to build up the hydrophilic part for surfactants. Among them, due to availability and quality, sucrose, glucose, and sorbitol are broadly used in industry. From sucrose (and sorbitol) and fatty acids, product mixtures are obtained, which are composed of mono-, di-, and tri-esters and are therefore relatively hydrophobic and only suitable for particular applications (e.g., as emulsifiers for foodstuffs and cosmetics or, in the case of the sorbitan esters, also in technical branches such as explosives and inverse emulsion polymerization).

Glucose, a reducing sugar, is derivatized selectively by acetalization with fatty alcohols to produce alkyl glucosides; *N*-methylglucamides are prepared by reductive amination with methylamine and subsequent acylation. Both products have proved to be highly effective surfactants in washing and cleansing agents, but only the alkyl glucosides are produced on an industrial scale at present. The alkyl glucosides have also additionally established themselves in the cosmetic products sector, as auxiliaries in crop protection formulations, and as surfactants in industrial cleansing agents and, as of today, are by far the most important sugar surfactants, when the annual production capacity is considered [14].

Cognis was the first company to introduce alkyl polyglycosides (C12/14 alkyl chain) on an industrial scale and at required product quality with a production capacity of approximately 50 000 tons/year (APG<sup>®</sup> surfactants). Other manufacturers include Akzo Nobel, BASF, Kao, SEPPIC, and LG. The manufacturing route is laid out in Scheme 4.



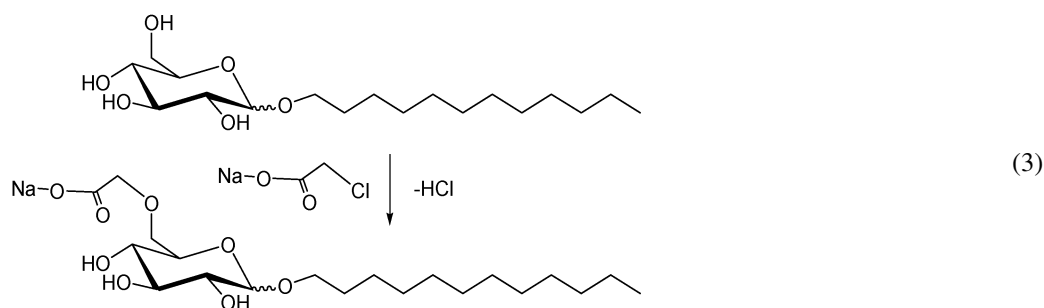
**Scheme 4** Manufacturing process for alkyl polyglycosides [2c].



Unique properties have previously been determined for alkyl polyglycosides, particularly in combination with other surfactants. For example, the use of alkyl polyglycosides in light-duty detergent or shampoo formulation means that the total amount of surfactants can be reduced without sacrificing any performance. Alkyl polyglycosides have a good compatibility with the eyes, skin, and mucous membranes and even reduce the irritant effects of surfactant combinations. On top of this, they are completely biodegradable, both aerobically and anaerobically. The relatively favorable classification (for surfactants) into class I under the German water hazard classification (WGK I) results from this.

#### Alkyl polyglycoside derivatives [15]

Alkyl polyglucoside carboxylate (INCI name sodium lauryl glucose carboxylate (and) lauryl glucoside, e.g., Plantapon<sup>®</sup> LGC SORB), is a new anionic surfactant with excellent performance for personal-care cleansing applications. In shampoo and shower bath formulations, the anionic surfactant shows a good foaming behavior. In body wash applications, it improves sensorial effects. Cosmetic applications include mild facial wash gels, mild baby shampoos, mild body wash for sensitive skin, wet wipes, and special sulfate-free shampoo applications. A new industrial process based on the reaction of sodium monochloroacetate with aqueous alkyl polyglycoside (without additional solvents) enables the manufacturing of this product in an economically and ecologically favorable way (eq. 3).



#### Polyol esters [12a,16]

Emulsifiers based on glycerol, polyglycerol, or other polyols, are a class of products which are well known in the market and used particularly in products for personal care and the food area. Polyglycerol esters are obtained by esterification of polyglycerol, which is produced by the oligomerization of glycerol under basic conditions with fatty acids. The properties of the various products can be adjusted by the type of polyglycerol used on one hand and by the chain length and type of the fatty acid used on the other hand (Table 6). For example, polyglyceryl-2-dipolyhydroxystearate (from polyglycerol and ricinoleic acid) is recommended to be used in body lotions. It leaves the skin with a smooth and non-greasy feeling, spreads easily, and absorbs quickly.

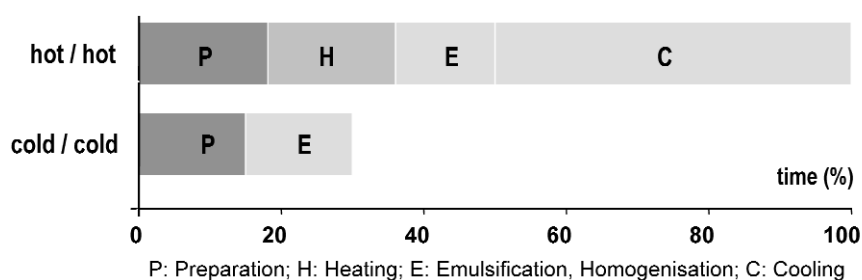
**Table 6** Properties of selected polyol esters as emulsifiers for personal-care and food technology.

INCI name	Application properties
Polyglyceryl-3-diisostearate	W/O emulsifier (typically $M_W = 725$ ; pale yellow liquid)
Polyglyceryl-2-dipolyhydroxystearate	W/O emulsifier for lotions and creams (typically $M_W = > 3000$ ; yellow, cloudy, viscous)
PEG-4-polyglyceryl-2-stearate	O/W emulsifier
Pentaerythritol distearate	Consistency wax with sensorial benefits
Polyglycerol stearate (E 475)	Food emulsifier
Polyglycerol polyricinoleate (E 476)	Food emulsifier

Based on pentaerythritol and stearic acid, pentaerythritol distearate has been recently developed. It is offered in the market as an off-white wax with very weak odor and is used as coemulsifier and consistency factor for a variety of cosmetic products.

*Multifunctional emulsifier compounds based on alkyl polyglycoside*

Requirements for modern emulsifiers are manifold, including easy handling in production processes, compatibility with modern emulsification techniques, and balanced sensory feeling. One example for such a multifunctionality is a compound based on glycerine, alkyl polyglycoside, and polyglyceryl-2-dipoly-hydroxystearate (e.g., Eumulgin® VL 75). In combination with selected emollients, it allows the preparation of oil/water (O/W) emulsions with high quality and stability (small droplet sizes). In addition, due to the liquid appearance of the product, and, as a consequence, the possibility for cold processing, the manufacturing time and costs for the preparation of emulsions are reduced along with significant energy savings (Fig. 3).



**Fig. 3** Capacity increase and energy savings by cold emulsification processes.

The intelligent combination of alkyl polyglycoside and glyceryl oleate resulted in a new product which combines emulsifying and cleansing properties with outstanding care effects, such as enhancing of the skin lipid layer. This effect is proven in a standardized test by washing the fore arm, rinsing, drying, and extracting the lipid layer on the skin with ethanol pads. The lipid content is measured by quantitative analysis of glycerol oleate in the extract. Typical application in the cosmetic market is as a multifunctional care additive in clear and pearlescent cleansing preparations [17].

### Emollients [18,19]

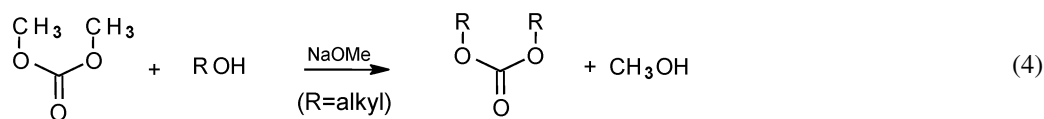
The physicochemical nature of the oil-phase components in a cosmetic emulsion, the emollients, determines their hair- and skin-care effects, such as smoothing, spreading, and sensorial appearance. Test methods have been developed to characterize and classify the numerous emollients available on the market, such as silicones, paraffin, and oleochemical-based products. The latter include glycerides, esters, alcohols, ethers, and carbonates with tailor-made structures depending on the performance needed (Table 7). However, especially with regard to additional effects, there is still a demand for new products and product combinations with unique performance properties.

**Table 7** Selected emollients.

Structure	INCI name
Ester	Hexyl laurate, coco-caprylate, hexyldecyl stearate Decyl oleate, oleyl erucate, caprylic/capric triglyceride
Guerbet alcohols	Hexyl decanol, octyl dodecanol
Hydrocarbons	Diethylhexyl cyclohexane
Ethers	Dicaprylyl ether
Carbonates	Dicaprylyl carbonate

For example, a compound based on dioctyl ether (INCI: dicaprylyl ether) from coconut- or palm kernel-oil-based octanol (e.g., Cetiol<sup>®</sup> LDO) allows the formulation of silicon oil-free hair-care products, particularly for the use as hair cleansing preparations in order to improve the tactile hair feeling and hair gloss. In combination with wax esters and cationic polymers, additional benefits like improved sensorial feeling are achieved.

One example of a new product type for skin care is dioctyl carbonate (INCI: dicaprylyl carbonate, e.g., Cetiol<sup>®</sup> CC). The product is synthesized by the trans-esterification reaction of octanol and dimethyl carbonate in the presence of alkali catalyst (eq. 4). Dioctyl carbonate is a dry emollient with excellent dermatological compatibility and a comprehensive performance profile, such as, solubilizing and dispersing ability for sun-care filters, and a unique sensorial feeling.



R. C. Guerbet in 1899 discovered the self-condensation reaction of alcohols, which, via the aldehyde as an intermediate, lead to branched structures (2-alkyl alcohols)—the Guerbet alcohols. [19] Starting from fatty alcohols from vegetable sources, such as octanol and decanol, the corresponding C16 and C20 alcohols are produced, 2-hexyl decanol and 2-octyl decanol. The reaction is carried out under alkali catalysis and high temperatures (>200 °C). Over the years, both products have proven to be efficient emollients in skin-care product formulations, but are also used for other applications, such as plasticizers.

## PERSPECTIVES

The successful development of environmentally compatible and powerful products in the sense of a sustainable development has been demonstrated by various examples of recent product innovations from oleochemistry. It can be assumed that in the future further possibilities for using renewable resources will be intensely investigated. Here, the combination of different types of vegetable raw materials, such as vegetable oils, carbohydrates, and proteins, to form new products and intelligent product concepts in order to meet market and consumer needs will be a challenge for research and development. However, regarding the future availability of natural fats and oils as the base raw materials for oleochemistry, this will depend on the scope of implementation of the Bioenergy and Biofuel Strategy as part of the Kyoto Protocol, too. The subsidized use of vegetable oils for bioenergy and biofuel production is completely contradictory to their established use in nutrition and to future developments of oleochemical-based products with high value added for industrial use. Therefore, edible oils and fats should not be part of this biomass regulation, and subsidies for biofuel and bioenergy in general should be more flexible.

(Petrofree is a registered trademark of Halliburton; Radiagreen is a registered trademark of Oleon; APG surfactants, Cetiol, Empol, Eumulgin, and Plantapon are registered trademarks of Cognis.)

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