SECOND EUROPEAN DETERGENTS CONFERENCE REPORT

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Detergent Polymers, Other Ingredients, Basics, Tests, Assessment of Sustainability und Environmental Evaluation

The Second European Detergents Conference embedded in the 53rd SEPAWA Congress took place in the Congress Centrum Würzburg, Bavaria, from October 11th–13th, 2006. More than 1320 attendees from 28 countries visited this event – this was an increase of about 10% compared to 2005.

In the jointly organised Sections *Raw Materials for Detergents*, *Basics for Detergent Chemistry*, *Product Enhancement by Detergent Additives*, *Evaluating Tests for Detergents*, *Assessment of Sustainability of Detergents*, and *Environmental Evaluation of Products*, 25 Lectures were hold. Moreover, in the SEPAWA Sections on *Formulating Cosmetics*, *Special Product Concepts for Cosmetics* and *Active Ingredients in Cosmetics* further 17 Lectures were given focusing on hair and skin care, natural actives, special product concepts and emulsifying agents. Special highlights of the Congress were the Keynote Adress of Free Democratic Party's (F.D.P.) Leader and Parliamentary Party Leader *Guido Westerwelle*, the traditional presentation of GfK's *Wolfgang Twardawa*, this time on "The Bermuda Triangle of Innovations" and the artistically arranged event "Share the Passion – The Perfume" by the German Society of Perfumers in the SEPAWA (DGP). Stimulated by the topical movie of *Patrick Süskind*'s book *The Perfume – History of a Murderer*, a fascinating show around perfume and passion was presented.

After the opening remarks of the Presiding Chairman of SEPAWA, Dr. *Lothar Rasthofer*, the Chairman of the GDCh Expert Group Detergent Chemistry, Dr. *Gregor Brodt*, said: "Without scientific progress and the thereby resulting innovations an industry cannot compete on the global market today. On the contrary, a lack of innovation would cause the industry to suffer a set back and the loss of many valuable jobs in Europe. We trust that we will be able to encourage scientific advancements and the implementation of newly presented ideas by means of this European Detergents Conference. Furthermore, it may help that the European detergents and cleaners industry will become more closely connected and thereby being able to be more competitive".

Detergent Polymers

Again this year, detergent polymers run like a thread through most Conference Sections such as *Raw Materials*, *Basics*, *Additives*, and *Performance Tests*. Because of the grow-

Creating a Free Society
Keynote Lecture held by Dr. *Guido Westerwelle*,
Chairman of the Free Democratic Party of Germany and FDP Parliamentary Leader in the Bundestag

"There must be an end to the state's economic bureaucracy", *Guido Westerwelle* pointed out. Germany needs a political change. Personal freedom before common equality, individual privacy before governmental regulation, and actively attaining before passively distributing are his commitments.

After strongly criticizing the economic politics of the ruling coalition, the FDP leader identified three challenges that Germany must still overcome in this globalized world: The demographic developments with a rapidly ageing population that leads to a competitive disadvantage in comparison to booming Asian countries with a younger population; second, the insufficient education and apprenticeship possibilities as well as deficits in research, and lastly the fiscal policies that should bring tax relief and thereby promote productivity. Too much state and too little personal initiative is one of the foremost constraints to a healthy development of our society and political system. "Our citizens should accept this challenge and get more involved in politics. We have to create a free society in order to take advantage of the possibilities globalization offers", said *G. Westerwelle* at the end of his speech that received great applause.

ing importance of theses ingredients for laundry and cleaning detergents the six Lectures focusing on this field are first summarised here. In this context, *T. Albers* (together with *M. Weuthen*), Cognis Deutschland GmbH & Co. KG, Düsseldorf, Germany, presented "Specialty Polymers for Household Cleaners – Perceivable Effects by Surface Modification". The performance of household cleaners can be approximately characterised by primary cleaning performance. Especially in recent years there is a demand for secondary cleaning effects, which makes cleaning easier, more efficient and longer lasting. The demand can be met by using polymers with surface modifying properties.

A modification of surfaces affects mostly the hydrophilic character and change the behaviour against water or soil. Cationically modified polymers show especially on highly energetic surfaces high surface affinity. Amphoteric polymers lead on different surfaces to amphiphilic behaviour, whereas the modification is depending on the surface energy of the original surface and the design of polymer.

Hydrophilically modified amphoteric polymers can decrease the contact angle especially on polar surfaces like glass and ceramic significantly. This leads to better wetting resp. spreading of water films.

Hydrophobically modified amphoteric polymers rises the contact angle on polar surfaces and can produce a water film, which flows down in very short time (Fig. 1). That way a quick drying is achieved. In particular hydrophobic amphoteric polymers can modify non-polar surfaces. These kinds of polymers provide a high efficiency and are applicable for long-lasting effects.

As visual effects an improved gloss, streakfree cleanliness, a quick and complete water drain, an easier to clean surface and a lower resoiling behaviour are achieved.

Polymers have been widely used in detergent and cleaning formulations. However, driven by the ever-changing market needs, formulators are constantly seeking for new polymers in order to improve the performance of their formulations. Therefore, a fast identification of a new polymeric additive and new product development is highly desired. In order to be able to achieve this, a sound understanding of how the polymer works, how the polymer structure affects its property and therefore the formulation performance needs to be acquired. *Yaqian Liu* (co-authors: *J. Detering, S. Behrens, S. Champ, G. Oetter, D. Boeckh* and *G. Brodt*), BASF AG, Ludwigshafen, Germany, promoted "Understanding the Role of a Polymer in a Detergent Formulation". This presentation focused on laundry applications and addressed three laundry-relevant questions, in order to illustrate how physical-chemical investigations can greatly help to gain insights on the role of a polymer in a laundry formulation. The three questions are: 1) how does a polymer improve soil removal; 2) which polymer to choose in order to improve the water hardness tolerance of anionic surfactants (how to boost anionic surfactants); 3) why does LAS reduce the effectiveness of PVP and PVP-co-PVI as dye transfer inhibitor? It is shown that with surface charge measurement and fluorescence spectroscopy with pyrene as a probe, it could be deduced that a certain nonionic polymer improves soil removal by triggering surfactant micelle formation at a lower concentration, as well as by reducing oil redeposition.

In the second example, turbidity titration and light scattering measurement were applied to identify a polymer, which improves the water hardness tolerance. Lastly, surface tension measurement was shown to indicate a complex formation between polymer and surfactant, and therefore helped to explain the observation of reduced effectiveness in dye transfer inhibition in the presence of LAS. In summary, this presentation aimed at showing that a smart choice of physical-chemical methods/experiments could greatly enhance the understanding of the role of a polymer in a detergent formulation and therefore speed up product development.

Both surfactants and polymers are important constituents of many formulations. In many cases the function of the surfactant is that of soil removal. *B. Lindman* (together with *T. Nylander* and *Yulia Samoshina*), University of Lund, Sweden, delivered an overview on "Polymer-surfactant Systems – Basic Interactions, Competition for a Surface and Relations for Cleaning". The cleaning effect of a surfactant depends critically on the surfactant chemical structure, in particular the balance between hydrophilic and hydrophobic parts; there is an optimum in performance when a certain so-called critical packing parameter has a value of one, corresponding to a spontaneous packing into planar layers. Often a polymer is added to a cleaning formulation to achieve additional benefits. The interaction between polymers and surfactants involves a combination of hydrophobic and electrostatic forces and can be attractive or repulsive. In case of attractive interaction as exemplified by oppositely charged surfactants and polymers, like the case of an anionic surfactant and a cationic polymer common in formulations, there may be an associative phase separation (Fig. 2). This leads to a concentrated phase of surfactant and polymer in equilibrium with a dilute solution. The behaviour of these mixed systems on solid surfaces is related to the phase behaviour. It is found that, depending on concentration, an ionic surfactant can either induce additional polyion adsorption or induce desorption. Kinetic control of adsorption and, in parti-

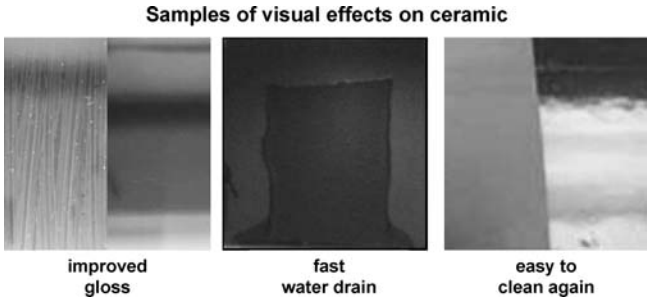

Figure 1 Surface Modification: Samples of visual effects on ceramic (*picture credit: T. Albers*, Cognis)

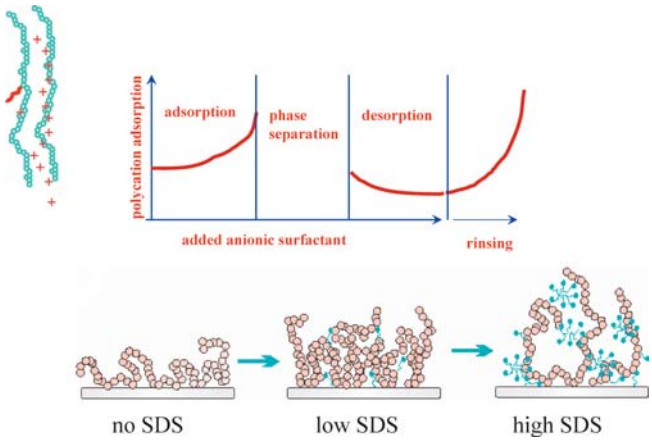

Figure 2 General trends of co-adsorption of cationic cellulose derivatives with SDS (*picture credit: B. Lindman*, University of Lund)

cular, desorption is typical. Important consequences of this include an increased adsorption on rinsing and path dependent adsorbed layers. Special attention is also put on the effect of hydrophobic modification of the polymer. There is in general a correlation between adsorption and associative phase separation as deduced from phase diagram work. Practical applications of interfacial polymer-surfactant interactions include as diverse areas as detergency and cleaning, hair-care, paints, coatings and gene therapy (Fig. 3).

"Synergies of Hydrophobic Polymers and Surfactants on Surface Activity and Cleaning Performance" were described by *M. Lang*[1] (co-authors: *Marie-Elise Chateau*[1], *K. Rodrigues*[2], *A. M. Carrier*[2] and *M. Antonietti*[3]), Alco Chemical, [1]Sempach Station, Switzerland, and [2]Chattanooga, TN/USA, and [3]Max Planck Institute for Colloid and Interface Research, Potsdam-Golm, Germany. The purpose of this Lecture was the evaluation of mutual interactions of hydrophobically modified polymers with different surfactants, potentially resulting in synergies effective in laundry applications. For this reason both academic research and primary detergency testing were conducted. The copolymers consisted of 30, 40, 50, 60 and 70 mol.% of acrylic acid with the balance being styrene. The surfactants are sodium dodecylbenzene sulfonate (LAS), sodium laurylethersulfate (AES) and alcohol ethoxylate (AE) with C_{13-15} and 7 EO. For the static interfacial tension measurements (25 °C) each of the polymers was added separately to the relevant surfactant at 10% inclusion level. In the case of LAS neither the critical micelle concentration – cmc (750 mg/L) nor the saturation surface tension (35 mN/m) were affected by the presence of polymers. However, below the cmc significant lowering of surface tension occurs, the polymer forms nucleation centers, from which surfactant entities smaller than a micelle are formed. The measurements with AES didn't show any significant changes below cmc (130 mg/L), so neither induction of aggregation or assembly formation took place, nor an interaction with small alkyl chains and styrene. Through distortion and hydrophilisation the saturation surface tension increases from 31.5 mN/m (packed alkyl phase) to 35 mN/m resulting in better solvatation of impurities into micelles, as they turn from very apolar (good for fats and oil) into medium polarity (good for dyes and hydrophilic soil). For AE the cmc (10 mg/L) and the saturation surface tension (28 mN/m) are very low and are not influenced by the presence of the polymer, which indicates that the polymer is not integrated into the hydrophobic part of the surfactant assembly. A switch of the curves at the cmc is relevant to a change in the micelle structure, resulting in an increase of solvatation capacity. In addition, a model emulsion using styrene as oily phase could be stabilised in the presence of polymer. The effects with LAS and AE discussed so far were re-evaluated regarding primary detergency in laundry machines, and in most cases the predictions for better results were confirmed. However, other formulation ingredients as well as washing conditions and type of garment influence the over-all performance. So there are many opportunities for future work to find out the most appropriate combinations as well as best conditions for (hydrophobic) polymers and surfactants combined in finished detergent formulations, not only in laundry!

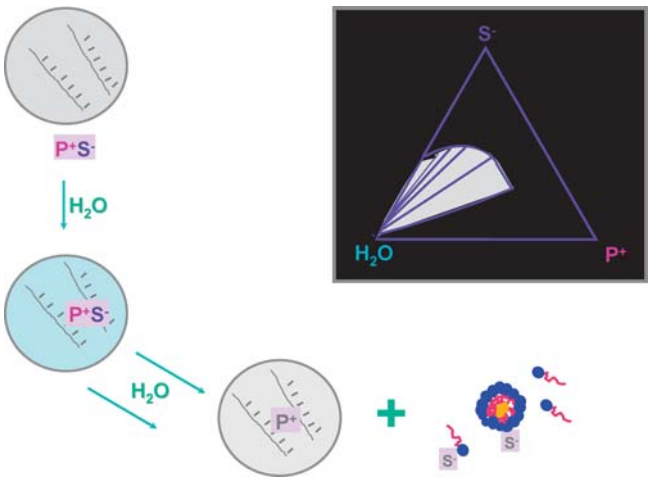

Figure 3 Polymer-surfactant applications (*picture credit: B. Lindman*, University of Lund)

S. Ugazio (co-authors: *B. Henault* and *Christel Simon*), Dow Corning S.A., Seneffe, Belgium, explained "New Ways to Process and Obtain Direct Incorporation and Stabilisation of Silicone Polymers in Fabric Conditioners". Rinse cycle fabric softeners (RCFS) have been first introduced on the US market in the late 1950's and became available in Europe in the 1960's. They aim to deliver softness, fragrance, static control, ease of ironing and fiber protection thus maintaining or restoring the initial feel of fabric during the rinse cycle of the wash cycle. Even if the main usage of silicone in the detergent industry is to provide effective foam control in consumer washing machines, this material has also largely been introduced to bring extra fabric care benefits when used in combination with classical fabric softeners. Dow Corning has been working in the recent years to identify and develop technologies to meet some of the above benefits when applied into fabric care formulations. It has been shown that when used in combination with fabric conditioning agents, softness improvements, ease of ironing, water absorbency and to a lesser extent, anti-wrinkle characteristic benefits have been demonstrated and commercially implemented.

Hence addition of silicone emulsions to fabric softeners have been used to deliver a variety of 'care benefits'. They are easy to handle and formulate and proved to be effective. However, their cost tends to prevent them from being broadly used in this application. Thus, with increased competition and higher raw material costs, fabric softener producers are looking for a more cost effective way to formulate silicones into their products.

To address this issue, Dow Corning has been working on direct incorporation of silicone polymers into quaternaries microstructure and has found way to obtain stable silicone entrapment while keeping application performance constant and final fabric softener physical properties acceptable (Fig. 4).

Polymers enable not only the enhancement of the viscosity of formulations but also its lowering as *H. Gümbel* (together with *T. Seebeck* and *R. Baur*), BASF AG, proved: "Special Polymers for a Highly Efficient Detergent Powder

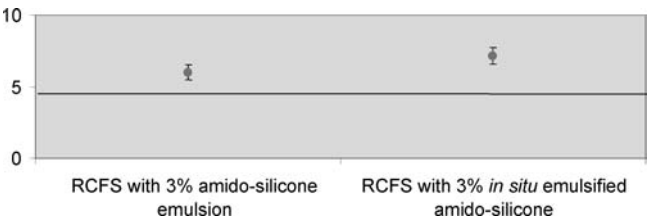

Figure 4 Softness performances of in-situ emulsified amido-silicone material versus the postaddition of emulsion of the same amido-silicone material. The black line represents the reference got when using the simple RCFS (*picture credit: St. Ugazio*, Dow Corning)

	Basis Zeolite 71 %	Basis STPP 75 %
Linear alkylbenzene sulfonate, Na salt	14	17
C13C15 Alcohol ethoxylate (7 EO)	7	6
Zeolite A (calc. as water-free)	22	
Sodium tripolyphosphate		16
Sodium metasilicate (calc. as water-free)	11	
Sodium carbonate	16	8
Sodium sulfate		27
Polymeric additive (active matter)	1	1
Water (total)	29	25

Table 1 Composition of detergent slurries (*source: H. Gümbel*, BASF)

Production". Polycarboxylates are essential components of powder detergents, not only as cobuilders. Aside from their impact in the laundering process they play an important role in the manufacture of detergent powders and tablets. They contribute to the adjustment of their morphology and their physical properties and they are of vital importance as a process aid already on the first stage of manufacturing, in the slurry preparation and spray drying.

Optimising the slurry preparation is crucial for the efficiency of the whole spray drying step. Due to its excellent performance in reducing the viscosity Sokalan® CP 44, a new modified polycarboxylate based on acrylic acid, allows to increase significantly the content of solid matter in a detergent slurry and to reduce the water content, respectively. This will result in substantial energy savings in the spray drying process. Further, the increased solid content will directly lead to an increase of the operational plant capacity of spray drying units at unaltered volumes of mixing vessels.

In the development of Sokalan® CP 44 the process of slurry preparation was simulated under well defined conditions in a laboratory test set-up. While stirring at 50 °C the powdered components are added in a controlled mode to the aqueous phase that contains anionic and nonionic surfactants and the polymeric test additive. The slurry is stirred further on at constant temperature and speed while the torque is continuously monitored. A sudden steep rise of the torque followed by an oscillating run of the curve indicates the loss of flowability of the slurry.

Comparing the performance of Sokalan® CP 44 with the actual market standard, copolymers of maleic and acrylic acid (MA/AA copolymer) with a molecular weight of approximately 70,000 D, immediately shows the advantage of the new polymer. Various tests have been performed using different slurry compositions. In both systems given in Table 1 the content of solid matter is more than 70 %, i. e. significantly higher than in current production practice.

Both in the phosphate-free composition based on zeolite and in the phosphate (STPP) based composition 1 % (a.m.) Sokalan® CP 44 yields a homogeneous, readily flowable slurry with relatively low viscosity. The effect of homogenisation and viscosity reduction is maintained for a period of 6 to 7 hours, only then an abrupt rise of the torque is observed and the slurry looses its flowability.

By contrast the reference product MA/AA copolymer 70,000 fails to yield a homogeneous slurry already right at the beginning of the test. The powder components don't get properly mixed in. Thus, no flowable mixture can be achieved as the immediate occurrence of a strong oscillation of the torque is indicating (Fig. 5 and Fig. 6).

Beyond its excellent performance as a process aid Sokalan® CP 44 features very good cobuilder properties in the laundering process as well. In phosphate-free laundry detergents polymeric cobuilders significantly contribute to the inhibition of fabric incrustation. Since many years maleic/acrylic acid copolymers 70,000 are the dominant standard type of polymer in this field of application. Fig. 7 shows the incrustation inhibition performance of Sokalan® CP 44 in comparison to MA/AA copolymer 70,000 in a phosphate-free detergent based on zeolite. The accumulated ash content on cotton fabrics was determined after 15 washing cycles at 60 °C.

The green line represents the ash content of a reference washing test without adding any polycarboxylate. 2.5 % MA/AA copolymer provide only a slight reduction of the ash level; with 5 % of this polymer the result gets much better. By contrast Sokalan® CP 44 yields a significant decrease of the ash content even with only 2.5 % polymer and outperforms the reference type at 5 % use concentration as well.

Combining the standard polymer with Sokalan® CP 44 in a ratio of 2 : 1 yields at a total polycarboxylate concentration of 3.75 % almost the same result as 5 % of the standard polymer.

Thus, combining Sokalan® CP 44 with prevalent cobuilders such as MA/AA copolymer 70,000 enables detergent manufacturers to reduce the total polycarboxylate concentration in powder detergents without suffering any performance losses.

Zeolite - based detergent slurry

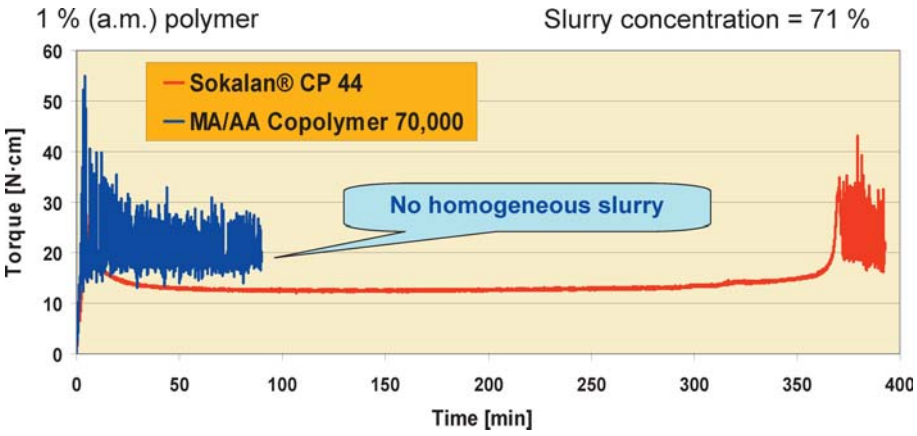

Figure 5 Viscosity progression in a zeolite-based detergent slurry (*picture credit: H. Gümbel*, BASF)

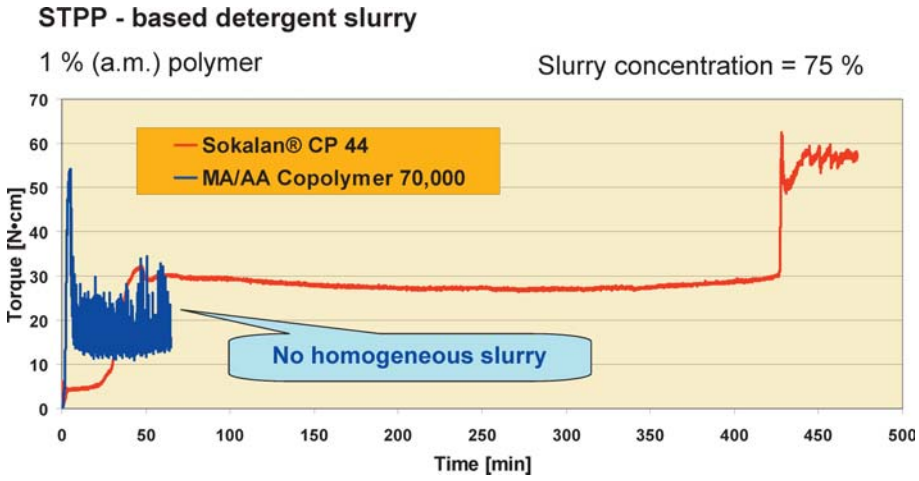

Figure 6 Viscosity progression in a STPP-based detergent slurry (*picture credit: H. Gümbel*, BASF)

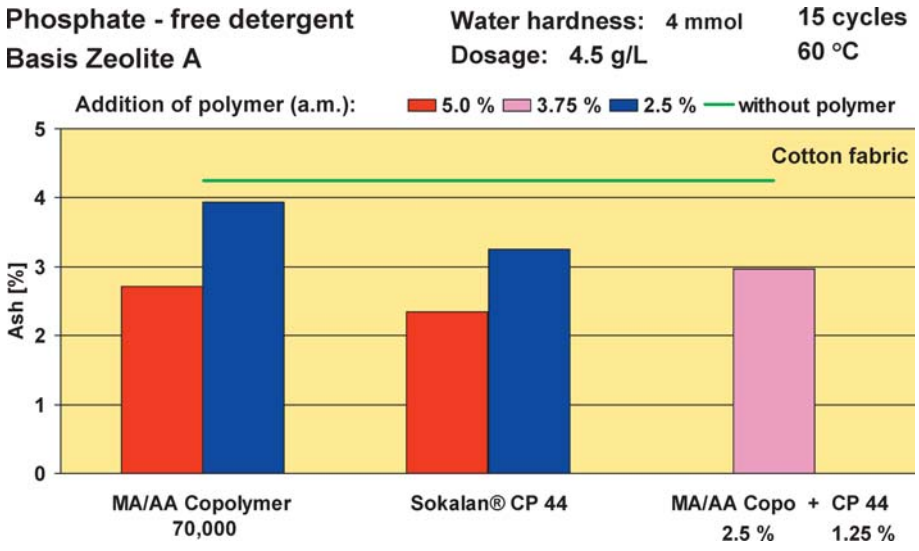

Figure 7 Cobuilder properties in the laundering process (*picture credit: H. Gümbel*, BASF)

Superspreaders, Fast and Mild Surfactants

In the first contribution of the programme, "Hydrolytically Stable Superspreaders" were recommended by *C. Roos*, GE Bayer Silicones GmbH & Co. KG, Leverkusen, Germany. Trisiloxane based superspreaders like Silwet* L-77 are a unique class of surface active materials. In addition to extraordinary wetting properties they provide a quick and lasting spreading action (Fig. 8), caused by a combination of aggregation properties and Marangoni effect. Water basically spreads on its own accord on surfaces until evaporation and lack of material flow due to thin film thickness terminate further expansion.

The combination of these properties made trisiloxanes successful especially in agriculture, where their use dramatically reduces the amount of water, herbi- and pesticides needed as a result of the better distribution. In addition the penetration into the leaves provides rainfastness. However, trisiloxanes are prone to decomposition under non-pH neutral condition. This reduced their applicability to applications, where the active is mixed in directly before use.

Now GE Silicones (GE Bayer Silicones in Europe and GE Toshiba Silicones in Asia Pacific) developed a series of new, hydrolytically stable superspreaders (HSSS). The new materials offer storage stability at wider pH-ranges: Y-17113 at pH 6 to 8, Y-17110 at pH 6 to 11 and Y-17112 at pH 2 to 11.

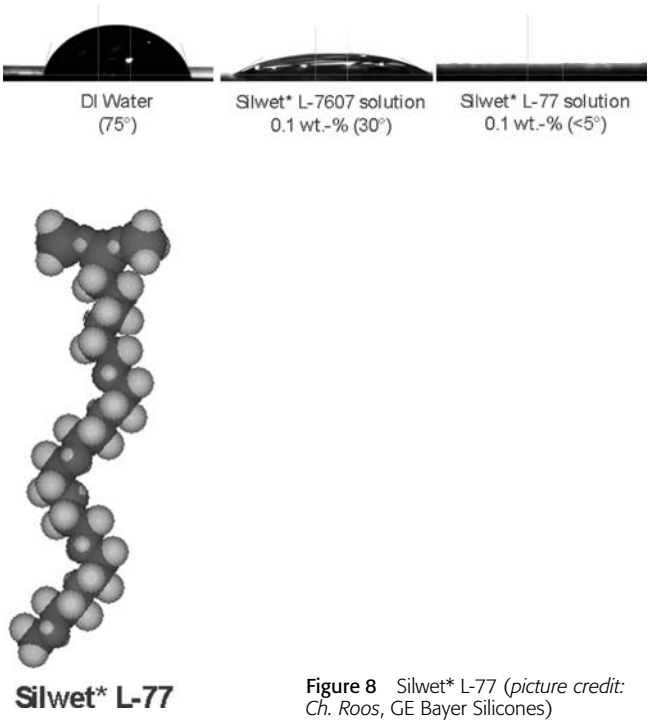

Figure 8 Silwet* L-77 (*picture credit: Ch. Roos*, GE Bayer Silicones)

This is proven by storage stability data of up to 1 year storage time, where the remaining actives concentration was followed by HPLC measurements.

These new grades offer a similar or higher potential to reduce the surface tension of water at add-on levels of 0.005 to 0.01 wt.% to levels below 25 mN/m like Silwet* L-77 and show excellent spreading performance on various substrates in a similar concentration range of 0.1 to 0.5 wt.%.

Besides spreading and wetting, which are properties usually associated with superspreaders, also durable antifog effects and improved penetration into porous substrates can be achieved.

The higher storage stability of these new products enables now the formulation of in-packaged products and expands the usage of the highly interesting superspreading effect into many new applications and formulations.

In virtually all surfactant applications there are process steps with high dynamics. The knowledge of properties of surfactants such as dynamic interface tension is a sound basis for better understanding and controlling of processes like wetting, cleaning, foaming, emulsification, etc. In this context, *H. L. Möhle*[1] (co-authors: *U. Aepli*[2] and *U. Ohlerich*[3]), [1]Kolb Distribution Ltd., [2]Dr. W. KOLB AG, both of Hedingen, Switzerland, and [3]Krüss GmbH, Hamburg, Germany, presented "Comparative Investigations of Adsorption Dynamics of Fatty Alcohol and Fatty Acid Alkoxylates".

After a survey on dynamic interfacial processes in industrial application (Table 2) and a compilation of methods characterising interfacial properties of surfactants the mechanism and modelling of surfactant adsorption were outlined. By means of processor tensiometer Krüss K 100 (static surface tension) and 'maximum bubble pressure technique' Krüss BP2 (dynamic surface tension) linear alcohol and fatty acid ethoxylates ($C_{10}EO_6$ and $C_{10/12}/EO_{10}$, respectively) were investigated as well as linear alcohol and fatty acid EO-PO/BO adducts (cloud point 1% in water: 35° and 45 °C, respectively; BO stands for butylene oxide).

Static surface tension data: The longer the hydrophobic chain the lower the cmc. The lower the surface area per molecule required the higher the surface tension reduction at equilibrium. Fatty acid alkoxylates show lower cmc.s than alcohol ethoxylates. EO-PO/BO adducts require more space than the corresponding ethoxylates.

Application	Time frame/conditions
Dynamic surface tension	
'Analytical' determination of surfactant concentration	1 ms to 10 s
Polymer dispersions in coating processes	10 to 100 ms
Agricultural spray application	Surface age 20 to 300 ms σ_d approx. 35 mN/m
Foam flotation – separation of minerals	10 to 1000 ms
Dynamic interfacial tension	
Water-based printing paints	Surface age 200 to 600 ms
Wetting of textile fibres, spin finishing	10 ms, $\sigma_d < 40$ mN/m
Emulsion explosives, stability prediction of w/o emulsios	γ_{dyn} @ 0.1 mL/h
Liquid-liquid extraction	Surface age 0.01 bis 10 s
Dynamic contact angle	
Wetting of tissue	0.001 bis 100 ms

Table 2 Dynamic interfacial processes in industrial application (*Source: H. L. Möhle*, Kolb)

Dynamic surface tension data: The numeric value of equilibrium properties like static or interface tension is only of limited importance for time-dependent processes. Processes in which 'new' interface is generated in fractions of a second are influenced by the dynamic behaviour of the surface involved, so the time function of the surface or interface tension is an important indicator. The fatty alcohol and fatty acid alkoxylates exhibit a similar shape of the measuring curves (Fig. 9). Different structural elements seem to be important and differences in surface tension reduction can be observed. Alcohol ethoxylates offer a surface tension reduction by a 20 mN/m at a surface age of 1 second, higher than that of fatty acid alkoxylates.

The diffusion coefficients were calculated according to the early-time approximation method. Between 20° and 60 °C the alcohol alkoxylates show higher diffusion rates than fatty acid alkoxylates. The diffusion coefficients of the EO-PO/BO adducts are higher than those of the corresponding ethoxylates. Since the diffusion coefficients are true molecular value and describe the real process they are tools to describe 'speed' in a scientific manner.

Results applying relaxation equation reveal that alkyl alkoxylates achieve the so-called meso-equilibrium state at a shorter time than fatty acid alkoxylates. Overall, alcohol alkoxylates show better performance dynamic surface tension reduction than the fatty acid alkoxylates.

A Lecture on "Amino Acid-Based Sarcosinate and Glutamate Surfactants", presented by *M. Husmann*, Schill & Seilacher AG, Böblingen, Germany, in one of the Cosmetic Sections of the Congress, should be mentioned here. In the early 1970's the social discovery of frequent body washing as a need of comfort and pleasure in combination with the skin irritation potential of the few available surfactants gave rise to increasing dermatological problems. This was the time when mild surfactants were required and amino-acid based surfactants were found as important key ingredient to solve these issues. presented.

Especially the mild sarcosinate surfactant Perlastan L-30 (INCI: Sodium Lauroyl Sarcosinate) and glutamate surfactant Perlastan SC (INCI: Sodium Cocoyl Glutamate, Disodium Cocoyl Glutamate) achieved most important influence in a broad range of applications like household and personal care. Many applications are related to their pronounced adsorption properties on proteinous materials, their foam forming power, biodegradability and physiological compatibility.

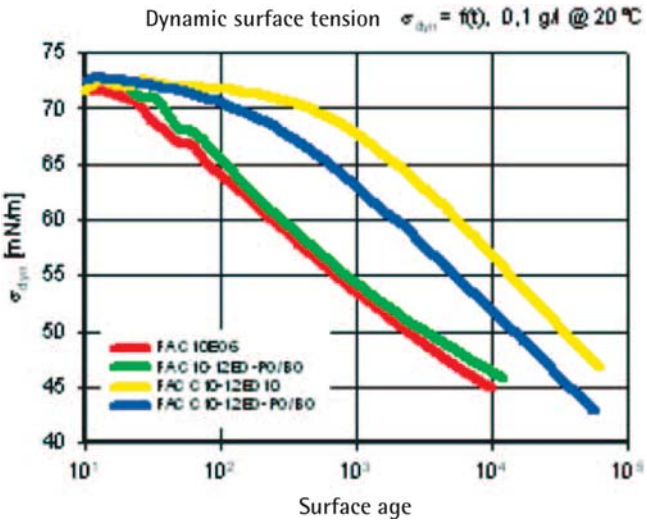

Figure 9 Dynamic surface tension data (*picture credit: H. L. Möhle*, Kolb)

Strong adsorption processes are responsible for care effects when skin is washed with soaps based on these mild surfactants. They readily adhere to skin and retard moisture loss from skin. This group of surfactants is also claimed to reduce irritation usually caused by severe components in formulations.

A further important factor for personal care application is their cleansing power under pH conditions close to the natural pH of the skin. Especially the two carboxylic groups of the glutamate surfactant Perlastan SC help the skin to maintain its natural acidity.

Outstanding adsorption properties on metal surfaces leads to metal corrosion inhibition properties of Perlastan OCV (Oleoyl Sarcosine) which opened up a broad field in industrial applications. This is originated by a five-membered ring where metal ions of the surface are coordinated through nitrogen and oxygen atoms of sarcosinate structure. The carboxylate moiety is orientated almost perpendicular to the surface and acts as protective hydrophobic shield with the thickness of a monolayer.

Novel Proteases

"Novel Proteases for the Growing Liquid Market in Europe with an Alternative to Boric Acid for Stabilisation in Liquid Detergents" were recommended by *T.L. Husum*[1] (together with *C. Ladefoged*[1], *Petra Salzmann*[2] and *E. Petiot*[1]), [1]Novozymes A/S, Bagsvaerd, Danmark, and [2]Novozymes Deutschland GmbH, Ingelheim, Germany. Consumers want liquid detergents and this rapidly growing market is estimated to be 16% of the total detergent market in Europe. A novel protease – Liquanase® – for this segment is now commercially available, supplementing Novozymes' long commitment to this field with the well known Alcalase® and Savinase® products. This new liquid protease demonstrates superior protein-fighting capabilities.

Aged and heat-treated blood, blood/milk and other protein stains are some of the biggest challenges for formulators in the development of effective laundry detergents. Tests show that Liquanase is particularly tough on blood stains. Like Alcalase and Savinase it delivers an exceptionally high level of general cleaning, which is a basic requirement for any laundry detergent. Laboratory tests have shown that Liquanase consistently outperforms the current proteases available in the market in removing stains containing aged blood, mixed meat and blood/milk, as well as a wide range of other protein stains (Fig. 10).

An important customer care-about for formulators is that the enzymes maintain their activity. Each enzyme must be sufficiently robust and the detergent must be formulated to protect the enzymes. Liquanase has an advantage over current proteases in the market because it is remarkably compatible with other enzymes during storage in a detergent, ensuring a long shelf-life.

This is demonstrated in Fig. 11, where the stability of the detergent amylase Stainzyme® is tested in the presence of Liquanase, Savinase and Alcalase, and without any protease. In addition Liquanase has also a very high compatibility with other enzymes like Lipex® (lipase), Termamyl® (amylase), and Endolase® (cellulase).

General stabilisation of enzymes in liquid detergents is seen as the biggest formulation challenge. In liquid detergents, the enzyme molecules may loose their activity during storage due to interaction with other detergent ingredients.

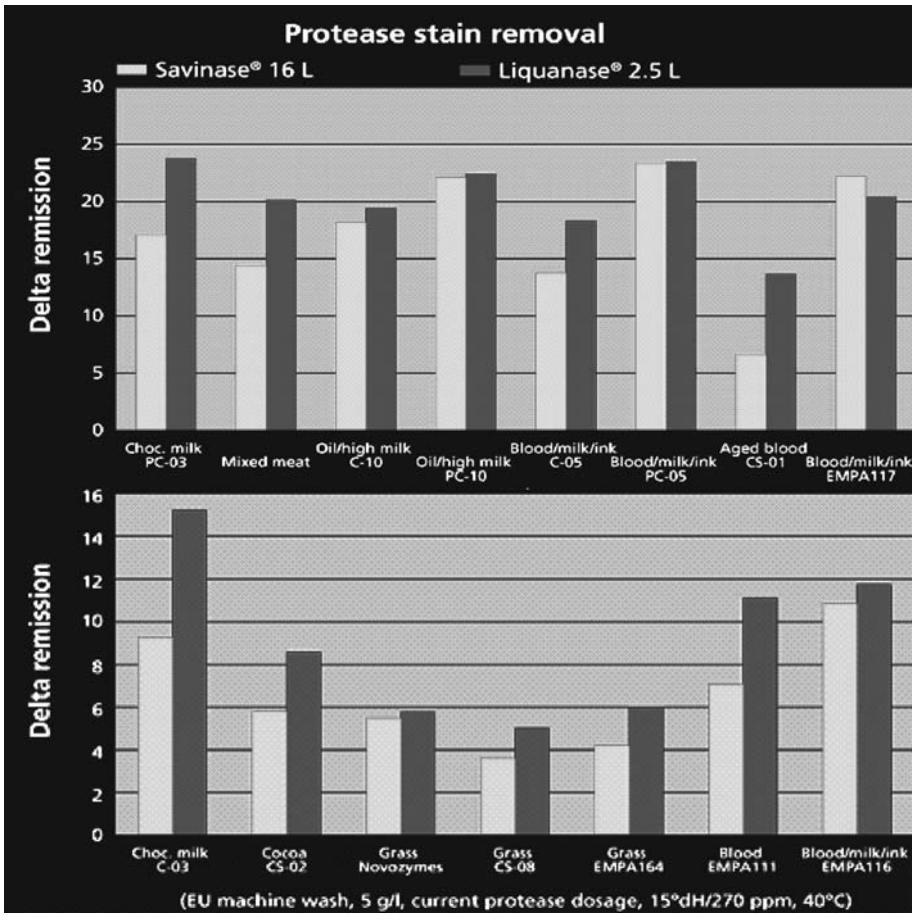

Figure 10 Protease stain removal: Liquanase is consistently superior to or as effective as existing proteases on a broad set of commercially available protein stains from various suppliers in commercial EU liquid laundry detergents (*picture credit: T. L. Husum*, Novozymes)

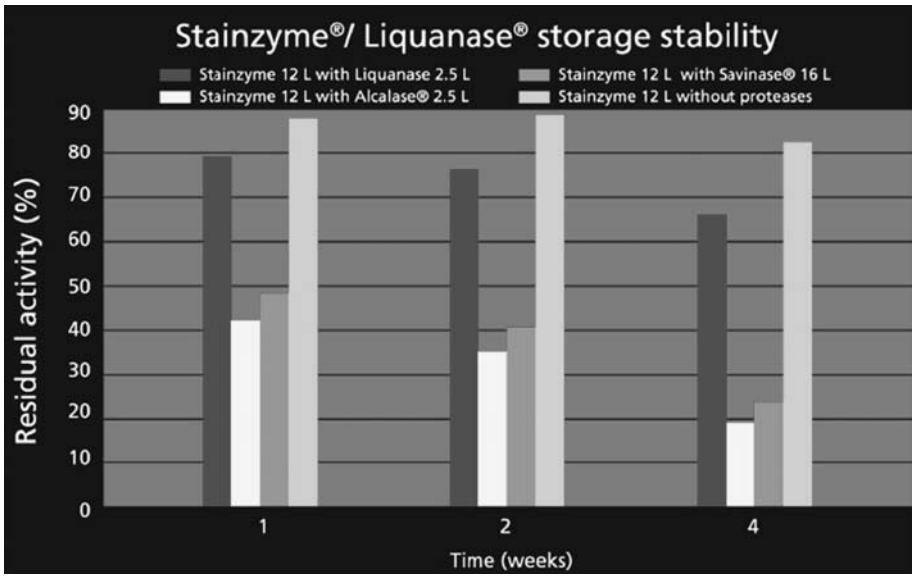

Figure 11 Liquanase Compatibility: Liquanase demonstrates remarkable compatibility with other enzymes when it is stored in detergents. Tests shown in this figure are for Stainzyme storage stability in detergents with Liquanase, Alcalase, Savinase and no protease (*picture credit: T. L. Husum*, Novozymes)

Another factor in liquid detergents is proteolytic breakdown. Prevention of proteolytic reactions is best managed by adding reversible protease inhibitors to the detergents. In traditional protease inhibition, borax has been the preferred reversible inhibitor, however, it has continuously been on the agenda of the European committee to potentially reclassify boric acid as a reprotoxic substance. This may lead to the conclusion that liquid detergent for the EU market might have to have a warning label on the packages.

An alternative stabilisation method is today available under the name ultra proteases. Instead of borax ultra proteases base their effect on a built-in stabilizer called 4-FPBA (4-formyl phenylboronic acid).

Ultra proteases are well-proven alternatives to proteases stabilised with boric acid and has been used as early as 2002, and are good choices for replacement of boric acid. Beside the general stabilisation benefit of the ultra proteases these products also offer some additional benefits.

Using ultra proteases might result in cost savings since there is no need to use boric acid, and at the same time manufacturers can reduce or eliminate the amount of polyols such as propylene glycol that are normally added to their formulations.

Methanesulfonic Acid – The 'Green' Acid

Methanesulfonic acid has many very useful chemical and physical properties. These properties are the reason why methanesulfonic acid has become established as the acid of choice in many different areas of application. *T. Heidenfelder* (co-author: *H. Witteler*), BASF AG, presented "Cleaning with Methanesulfonic Acid – A Solution for Many Problems!"

Cleaners are assessed according to ecological, toxicological and safety criteria as well as their cleaning performance. Methanesulfonic acid is much more effective for dissolving deposits such as calcium carbonate scale than many other acids, including hydrochloric acid, sulfamic acid and citric acid. Calcium carbonate scale can be dissolved more quickly with mixtures of methanesulfonic acid and sulfamic acid than with either of these acids alone. Because methanesulfonate salts are highly soluble, methanesulfonic acid is very effective for keeping non-metallic and metallic cations in solution, which ensures efficient cleaning. Methanesulfonic acid is odor-free and has a low vapor pressure, which provides wide scope for devising formulations and also has a number of other advantages from the point of view of safety and environmental protection. It is also miscible with water in all proportions and it is resistant to hydrolysis, colorless and readily biodegradable. It has been described as a 'green' acid in some areas of application on account of its ecological advantages.

Because of its unique properties, methanesulfonic acid has established itself in the chemical and pharmaceutical industries, and it is now quickly gaining in popularity in the cleaners industry. The trend towards using methanesulfonic acid instead of established acids such as hydrochloric acid, phosphoric acid and sulfamic acid is new, but the simple reason for this is that methanesulfonic acid has only been available in sufficient quantities and in sufficiently high quality in recent years.

$$H_2 + 2\,CH_3OH + 2\,S \rightarrow CH_3{-}S{-}S{-}CH_3 + 2\,H_2O$$

$$\underline{CH_3{-}S{-}S{-}CH_3 + {}^1/_2\,O_2 + H_2O \rightarrow 2\,CH_3SO_3H}$$

$$H_2 + 2\,CH_3OH + 2\,S + {}^1/_2\,O_2 \rightarrow 2\,CH_3SO_3H + H_2O$$

In the new, continuous process that has been developed and patented by BASF, dimethyldisulfide (DMDS) is synthesized from sulfur, hydrogen and methanol. The DMDS is purified by distillation and oxidized with air in the presence of a catalyst to yield methanesulfonic acid and water. The acid is then refined by distillation, which guarantees that Lutropur® MSA, the methanesulfonic acid supplied under the BASF trademark, fulfils unsurpassed standards of purity.

The New Dimension: Performance and Design

'A clean toilet is the most important sign of a clean home', one says. The psychological factors of bathroom and toilet cleaning are much more complicated than one might imagine. Fragrance and preventative maintenance cleaning effects support consumers understanding of a clean toilet. On the innovative cleaner market for rim blocks beside the targets cleaning and care a new dimension will be opened. In this context, *M. Lüken* (together with *J. Josa* and *Ralph Butter-Jentsch*), Henkel KGaA, Düsseldorf, analysed "Toilet Rim Blocks – Get Consumers Inspired".

In the past, toilet cleaning was achieved by using a brush and appropriate chemicals. To maintain the cleanliness of the toilet bowl after each flush, many products have been developed. These include products which can be placed inside

Figure 12 Performance & Design: Duo Active Alessi FreshSurfer and WildKayak (*picture credit: M. Lüken*, Henkel)

the toilet tank, or those which hang under the rim of the bowl. New innovations and developments continue to be launched to fulfil consumer's needs.

Recently a new dimension has been discovered: *Performance & Design*. The Duo Active Alessi FreshSurfer and the new Alessi WildKayak (Fig. 12) are the first toilet rim-blocks combining both benefits. The successful Duo Active Twin Tank solution developed in the beginning of this century is the basis for these developments. The new products are able to fulfil the consumer's demands of cleaning and fragrance performance on the one hand, and an attractive, artistic design on the other.

Basics: Synergism of Geminis, QSPR Computer Simulation, and Vesicle Gels

'Gemini surfactants' are a new class of amphiphiles with a particular property profile. They are best described as surfactant dimers (1), i. e. as intermediate structures between standard monomeric surfactants and polymeric surfactants. They consist of two surfactant units chemically linked via the head groups by a spacer group, which can be varied, e. g. according to its chemical nature or length. Gemini surfactants may exhibit improved properties or particular combinations of properties (2). "Structure-property Relationships of Gemini Surfactants and Synergism with Hydrotropes" were given by *L. Watteblad*[1] (co-authors: *Carine Note*[1] and *A. Laschewsky*[1,2]), [1]University of Potsdam, Golm, and [2]Fraunhofer Institute for Applied Polymer Research, Potsdam, Germany. Two new series of cationic Gemini surfactants with low Krafft temperatures based on the trialkyldodecylammonium chloride motif were investigated, with respect to key surfactant properties such as surface activity and foaming (3–5). The influence of the dimerisation and of the spacer group on the properties was examined in order to establish structure-property relationships. Two isomeric series of rigid spacer groups (aliphatic and aromatic) permit to tune precisely the distance separating the ammonium head groups while keeping the hydrophobicity constant within a given series. The dimerisation decreases strongly the critical micellar concentration (cmc), which is true on molar basis and on weight basis (3). Shorter spacer groups involve slightly lower cmc as well as reduced surface tension at the cmc, suggesting a tighter packing of the alkyl chains at the surface. More hydrophobic spacers reduce the cmc values somewhat, too. Concerning the foaming behaviour of aqueous solutions, the spacer length is a key parameter

Basic Research Award to *Claudio Cinquemani*
(Promotional Prize "Basic Research Detergent Chemistry")

On the occasion of the 2nd European Detergents Conference in Würzburg, the Chairman of the Expert Group Detergent Chemistry of the German Chemical Society (Gesellschaft Deutscher Chemiker – GDCh), Dr. *Gregor Brodt*, awarded this year's Promotional Prize "Basic Research Detergent Chemistry" to

Dipl.-Ing. *Claudio Cinquemani*

honoring his work on "Inactivation of microbes using compressed carbon dioxide – An environmentally friendly disinfection process". In his very systematically performed studies, *C. Cinquemani* has achieved new knowledge for a new cleaning and disinfection process using compressed carbon dioxide. The scientific significance and originality of his research are reflected by the interdisciplinary approach and the innovative method development. The results may give a basis especially for the cleaning and disinfection of medical textiles und therefore exhibit a high application link.

Claudio Cinquemani, born 1976 in Erbach, Germany, studiedEnvironmental Protection at the University of Applied Sciences, Bingen, Germany, and at the Universitat Autonòma de Barcelona, Spain. He achieved his diploma degree with a thesis on "Mercury removal with impregnated carbon: Design, construction and initiation of a model adsorber" conducted at the Fraunhofer Institute (FI) for Environmental, Safety and Energy Technology (UMSICHT), Oberhausen, Germany. In 2001, *Claudio Cinquemani* joined the FI UMSICHT, first in the Dept. Adsorption/Gas Cleaning and then as a project leader in the Dept. Biotechnology focusing on enzymatic reactions in supercritical fluids. From 2002 up to 2004, he was as a freelance worker also active for the Publisher of *Chemical Engineering and Biotechnological Abstracts* (CEABA-VTB – Verfahrenstechnische Berichte). From 2004 to 2006, he performed postgraduate work at the University of Auckland, New Zealand, and was graduated as a Master of Environmental Engineering (honours degree). Since 2004, he is a research engineer and responsible for the microbiological work at the German Centre for Textile Research North-West e. V. (DTNW), Krefeld. Presently, heprepares his doctorate thesis.

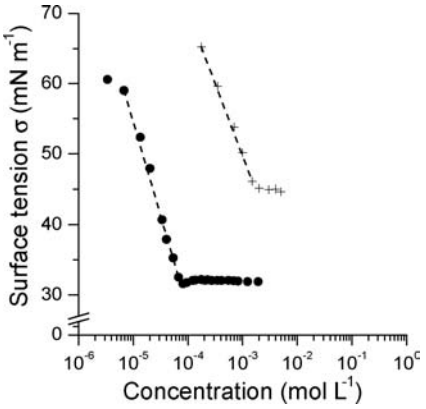

Figure 13 Surface tension curves of dimer EO-2 (EO-2 stands for Bis-2,2′-(dodecyldimethylammonium)-diethylether-hydrochlorid) and of a mixture of the latter with sodium salicylate (1 : 2 molar ratio): (+) EO-2, (●) EO-2 $(salicylate)_2$ (*picture credit: L. Wattebled*, University of Potsdam)

for tuning the foam stability of surfactant solutions: Gemini surfactants with short spacer group produce much more stable foams than those with long spacers.

The addition of organic salts (also called hydrotropes), such as sodium salicylate, vinylbenzoate or tosylate, to the Gemini surfactants markedly modifies the solution properties and aggregate morphology. Surface tensions and critical aggregation concentrations can be markedly reduced compared to the surfactants in the pure state (Fig. 13). This makes such mixtures advantageous, e. g. for wetting processes and for the solubilisation of hydrophobic compounds at low surfactant contents. Remarkably, the observed synergism is much more pronounced for Gemini surfactants than for analogous monomeric surfactants when combined with the same hydrotropes. Moreover, dimeric surfactants with an appropriate spacer group produce viscoelastic solutions after addition of certain organic anions. Surprisingly, this occurs for Gemini surfactants bearing alkyl chains as short as dodecyl, whereas no effect is observed when involving the 'monomeric' analogs. The viscosifying behaviour is present already at low concentrations, and reflects a marked growth of the micelles. Rheological measurements revealed a Maxwellian behaviour characteristic for entangled wormlike micelles.

Noteworthy, dimeric surfactants with a short hydrophobic spacer allow the micelle growth with usually inefficient organic salts such as sodium benzoate. Perspectives for the further use of dimeric surfactants include mixtures with oppositely charged conventional surfactants. For example, some mixtures with the oppositely charged SDS gave rise to vesicular aggregates, not observed for mixture of the monomeric analog and SDS under the same conditions.

H. Kuhn, CAM-D Technologies GmbH, Essen, Germany, presented "The QSPR Computer Simulation Method for Optimising New Surfactant Systems and Formulations of Detergents and Cleaners". The theoretical Quantitative-Structure-Property-Relationship (QSPR) method is a specific Molecular Modelling technique which is currently widely used in Material Science research projects. The application of these tools in industrial research and development yields to the rapid development of new surfactants, micro-emulsions and formulations for cosmetics and detergents. In principle, with QSPR it is possible to correlate physicochemical properties and the performance of surfactants with their molecular structures. Therefore, nowadays it is relatively easy to optimise foam boosting effects of surfactants with computer calculations. Furthermore, QSPR prediction models can be generated to estimate toxicological and environmental effects as well as potential hazards of new surfactants for body and skin in cosmetic applications.

In order to correlate molecular properties with experimental data of surfactants, statistic tools are required. Beside Neural Networks modern Genetic Function Algorithms are used. These methods are superior to classic statistics. If informations about the prices of the formulation ingredients are available, it is even possible to optimize formulations with commercial constraints. In summary, by the combination of QSPR and laboratory experiments surfactants can be designed more effectively and straightforward with the result of a more cost-effective industrial research and development process.

"Vesicles and Vesicle Gels – Structure and Solubilisation Properties" were presented by *M. Gradzielski*, Technical University (TU) of Berlin. Surfactant molecules may form many morphologically different structures, such as spherical or rodlike micelles, bicelles, or vesicles. Vesicles are closed amphiphilic bilayers, which on average have a spherical shape and can be subdivided into small (SUV; R = 4 to 20 nm) or large unilamellar vesicles (LUV; R = 50 nm to 10 µm) and multilamellar vesicles (MLV) (for phospholipids called liposomes), where one has a number of concentric vesicle shells, i. e. a structure that due to its similarity to onions is also called 'onion-phase'. As a general tendency one finds that unilamellar vesicles are more likely observed for dilute systems while multilamellar vesicles are more likely to be found for more concentrated surfactant systems. One way to control the flow properties of aqueous systems is by means of forming vesicle gels. Vesicle gels are obtained for a dense packing of vesicles which can be either unilamellar or multilamellar (Fig. 14). Typically, the shear modulus of vesicle gels is simply proportional to their packing density, given by the number density ^{1}N, via: $G_0 = \chi^1 \cdot N \cdot k \cdot T$, where χ is a factor accounting for structural details, such as the stiffness of the lamellae and the interaction of membranes (e. g. for multilamellar vesicles).

Of course, an interesting question is how to control the rheological properties of a vesicle system by its molecular composition. A particular system studied by the author and his group is that of the nonionic surfactant $C_{12}E_4$ that is known to form bilayer structures already in the dilute case and over an extended range of concentrations. The group employed a technical grade version of $C_{12}E_4$ known as Brij30, and for this system vesicle gels are formed in the concentration range of 5 – 25 wt.% of surfactant. The observed elastic moduli and the yield stress can be modified by the addition of small amounts of ionic surfactant that becomes incorporated into the amphiphilic bilayers. Due to the charging the repulsive interaction between the bilayers is increased, which leads to a substantial increase in the shear modulus of the gels. A maximum is observed for about 3 – 5 mol.% of surfactant substitution by a cationic or anionic surfactant. This rise of the elastic properties is very

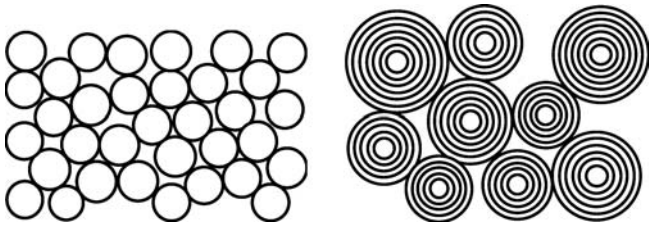

Figure 14 Schematic drawing of unilamellar and multilamellar vesicle gels (*picture credit: M. Gradzielski*, TU Berlin)

pronounced as the shear modulus increases by a factor of 10 to 50 due to the addition of this relatively small amount of ionic surfactant.

Another parameter on which the elastic properties depend crucially is the total concentration of amphiphilic material in a vesicle gel. For instance, for Brij30 based surfactant gels, with 4 mol.% substitution by the anionic Texapon N70, the shear modulus increases largely by increasing the total concentration of amphiphile and can be described by the following scaling law:

$$G = A * (c - c_0)^{\alpha}, \text{with } c_0 = 76\ \text{mM} \quad \text{and} \quad \alpha = 1.87$$

This means that gelation is occurring as low as at 76 mM, which corresponds to a weight concentration of 2% surfactant.

Thus, the rheological properties of vesicle gels are to a large extent controlled by

- the total concentration of surfactant and
- the charge density of the amphiphilic bilayer.

Therefore a systematic control of the flow behaviour is possible by properly choosing the molecular composition.

From Softeners to Fabric Conditioners

Konstanze Mayer (together with *R. Jeschke*), Henkel KGaA, outlined the development "From Softeners to Fabric Conditioners – A Category on the Move". First the economic situation of fabric conditioners in its various markets was presented. Although sales figures in most countries are rather constant for this category, there are several countries (e.g. Mexico and Japan) where the market grows significantly. Reasons for this growth are smart innovations. Huge deviations in per capita consumption between the countries suggest room for further growth.

Second the ecological situation of fabric conditioners was described. Today's softeners based on esterquat technology can be considered environmentally safe. A Life Cycle Analysis shows positive effects when using softeners due to a reduced drying and ironing time.

Launch activities of the last 10 years were reviewed. Launches can be clustered into four groups. The first group consists of products claiming technical benefits like easy ironing, quick dry or easy rinse. A second important class are sensitive products. These products contain selected ingredients for sensitive skin and are recommended by leading dermatologists. Products having new aesthetics form the third cluster. Examples are clear softeners or single dose softeners. Latest developments are products with new fragrance technologies as there are softeners with perfume microcapsules or the new range of aromatherapy conditioners.

Threats for the future of the fabric conditioner category will result mainly from new trends in the textile industry. Special garments using moisture management technology, stain protection technology or antibacterial treatment are available. The care labels of these garments typically recommend not to use fabric conditioners. Also for textiles with permanent softness no external softener is suggested.

Growth opportunities for this category will be based on a better understanding and meeting of consumer needs. One example is the increasing desire for a nice and long-lasting scent. Intelligent fragrance management will help to avoid huge losses of perfume during washing and drying in order to provide consumers with the scent when needed. Having the right composition of softening agents as well as optimising their adsorption will help to offer high-performance solutions at low cost.

Performance Assessment of Detergents

"Nonionic Surfactants and Their Emulsification and Cleaning Power – How the Hydrophobic Structure Influences the Properties?" asked *U. Steinbrenner* (together with *J. Tropsch* and *R. Baur*), BASF AG. Emulsions are widely used in both industry and daily life. In laundry, cleaning and dish wash oily dirt and grease must be emulsified and stabilised in water. Cosmetic creams and lotions as well as formulations and concentrates applied in e.g. agro, metalworking, textiles and leather industry require the formation of emulsions.

It has been known empirically for decades that surfactants based on branched hydrophobes offer additional emulsion stability compared to linear systems. Using methods developed in BASF to determine emulsion stability it could be quantified that ethoxylates based on Y-shaped hydrophobes, e.g. the iso C_{13} oxo alcohols of the Lutensol® TO range or the C_{10} Guerbet alcohols of the Lutensol® XP range, offer up to 100 times better stability against coalescence with respect to the corresponding ethoxylates based on linear hydrophobes.

In a second step, combinations of nonionic surfactants were tested for their use in emulsification. In opposite to the common understanding, surprising additional benefits have been detected by using the right components: The optimum with respect to good emulsion stability, fast wetting and low gelling is a combination based on ethoxylated C_{10} Guerbet alcohol and ethoxylated hydrophobes of high molecular weight.

Because of its connection with emulsion technology two Lectures from the Cosmetics Section are also summarised here. "A Novel Technology for the Cold Production of PEG-free, Small Particle and Low Viscous o/w Emulsions", was presented by *J. Meyer* (together with *Gabriele Polak* and *P. Hameyer*), Degussa AG, Essen, Germany. PIC emulsions are nanoemulsions prepared in a simple process without using a homogeniser, without a heating step and without the need to use ethoxylated emulsifiers. Such nanoemulsions are prepared in a transitional phase inversion process by just diluting an adapted oil phase with water with gentle stirring. Such an oil phase consists of an emollient, a combination of PEG-free emulsifiers and a co-surfactant. While the oil phase is diluted with water, a microemulsion-like phase with extremely low interfacial tension is passed in the phase inversion region (PIC: phase inversion concentration). Nanoemulsions are spontaneously formed by this phase inversion process during the dilution process (Fig. 15). As the well known preservative phenoxyethanol can be used as co-surfactant, such PIC emulsions offer an extremely easy-to-handle process producing PEG-free nanoemulsions with excellent long-term stability. Such emulsions can be used for e.g. impregnating lotions for cosmetic wet wipes.

H. Seidel, S. Black GmbH, Duisburg, Germany, recommended "Novel Glycerol-modified Silicone Emulsifiers for the Production of Stable o/w Emulsions". The acceptance of ethoxylated silicon emulsifiers in suncare formulations is reduced because of skin irritation potentials. By the replacement of polyethylene glycol chains with polyglyceryl-3 units, new nonionic emulsifiers are obtained (Fig, 16).

W/o-lotions with high water contents and with lowest viscosity values exhibit light and comfortable skin feel properties. By using polyglyceryl-modified silicon cross-polymers, low viscous w/o-emulsions with 90% internal phase are feasible (HIPR high-internal-phase-ratio-emulsions). The emulsion droplets are stabilised by steric hindrance of polymer emulsifier layers surround the droplets.

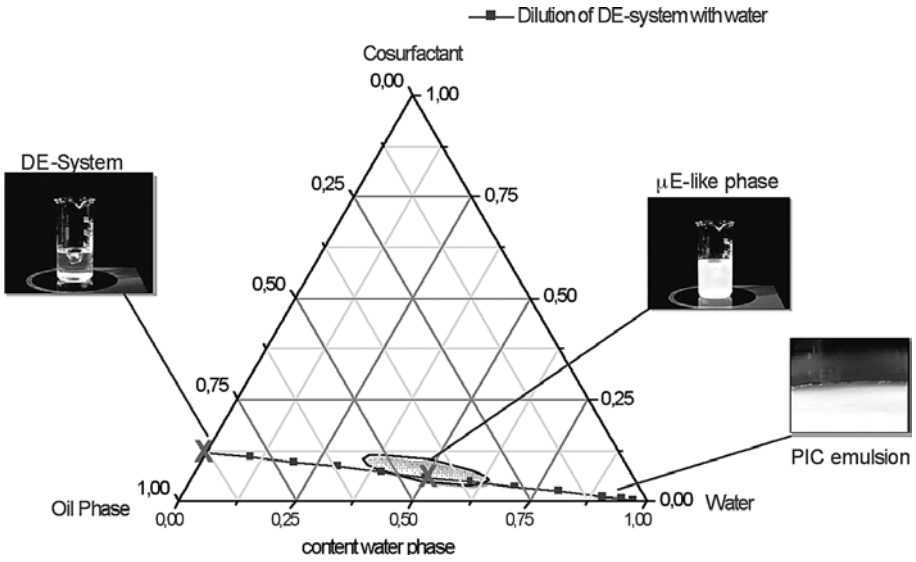

Figure 15 Phase inversion process in the DE-system (*picture credit: J. Meyer*, Degussa-Goldschmidt)

The extraordinary light skin feel properties of these silicon emulsifiers can also be used for the manufacturing of highest SPF suncare formulations loaded with about 30% of pigments (SPF 50+ according to FDA). For long-term stability improvement a combination of both polyglyceryl-modified silicon cross-polymer (KSG 810 and its branched version (KF 6105), is recommended.

The "Drying Performance of Automatic Dish Detergents" was assessed by *Sabine Both*[1] (together with *Corinna Böhme*[1] and *Britta Rummler*[2]), [1]Cognis Deutschland and [2]University of Bonn, Germany. Convenience is one of the most important topics in the household area. In this respect, the cleaning of fabrics, hard surfaces, and dishes at home should be quick and easy for the consumer. Regarding automatic dishwashing products this means combining the cleaning, rinsing and water softening by adding special surfactants and polymers to the formulation which enable spot-, film-free and dry dishes out of the dishwasher.

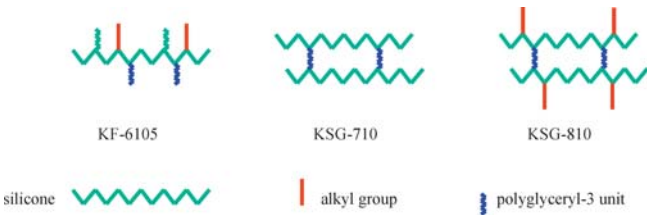

Figure 16 New nonionic silicone emulsifiers (*picture credit: H. Seidel, S. Black*)

To assess the drying performance of different products, a test method has been established, which provides information about the remaining water drops and streaks on the dishes.

To enable consumer-relevant conditions a normal household dishwasher is fully loaded with different types of dishes and cutlery made of porcelain, glass, stainless steel, and plastic. Also a ballast soil is added to the dishwasher during the cleaning cycle. At the end of the washing programme the assessment is started immediately. The remaining water droplets on each piece are counted in order to offer specific information about water resistance on each type of substrate in the machine.

It is possible to evaluate and differentiate the drying behaviour of dishes in dependence of the used automatic dish detergent with the proposed method. The drying performance of most multifunctional products is worse than the performance of the classical addition of rinse aids (Fig. 17). Especially plastic substrates show this effect

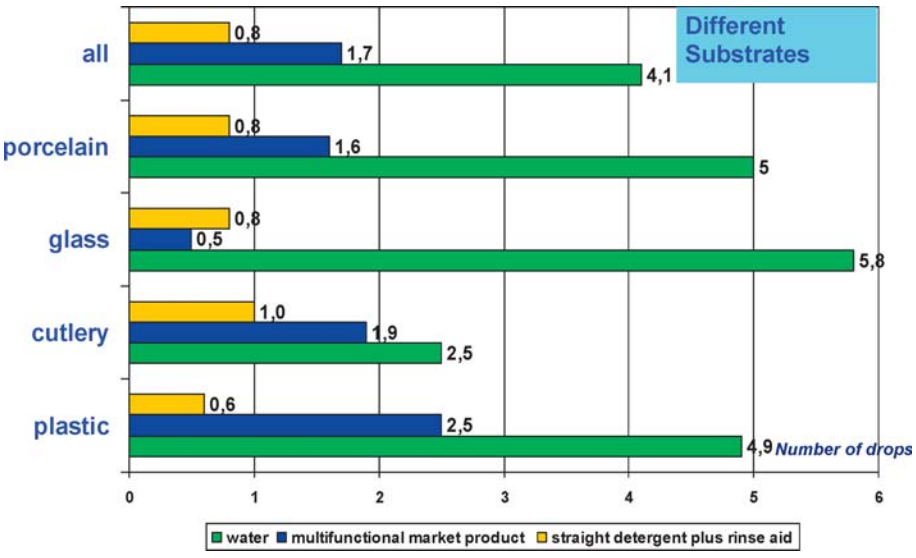

Figure 17 Drying performance for different substrates of ADD Market Products (*picture credit: Sabine Both*, Cognis)

clearly. With glass the drying performance of multifunctional and classical rinse aid products are similar.

However, this method is quite elaborate. For new product development new screening methods are needed to get information fast and as reproducible as with the proposed procedure.

If the drying temperature is decreased the performance of drying is also decreased. A task for future product development will be to gain the same rinse and drying effect on the dishes while saving energy (lower temperatures) as well as to get a better understanding of the interaction of dishwashing machine technology and chemistry.

C. Rudolph (co-author: *S. Liebsch*), Zschimmer & Schwarz Mohsdorf GmbH & Co. KG, Burgstädt, Germany, delivered an "Evaluation of the Sequestering and Dispersing Power of Additives under High Thermal and Salinar Stress". Both the quality of water and the application temperature have high impact on the performance of cleaning processes. High concentrations of dissolved ions (especially alkaline earth metals but also transition metals and silicates) and high temperatures support the undesired pathway to the formation of scaling on surfaces and aggregates.

A simple and easily applicable method for the evaluation of the sequestering and dispersing power of additives has been developed, providing reproducible information within short times under omission of highly sophisticated and costly analytical techniques. Provided that the system being investigated allows to discriminate the samples by a visual inspection in terms of turbidity and/or precipitation, the performance rating is only based on the degree of those parameters. The compatibility of the discussed method with more sophisticated titration techniques is demonstrated and additional information on the agglomeration and sedimentation behaviour becomes available.

The investigations and results on supersaturated solutions of calcium carbonate in the presence of defined background concentrations of other electrolytes at different temperatures under static and dynamic conditions are presented in detail, focusing on highly alkaline conditions (pH = 12). The additives tested (amino-polycarboxylates, phosphonates and polymers) show very clearly performance differences with decreasing application concentrations whereas those differences grow significantly with increasing temperatures. These findings can be explained by the different anti-scaling mechanisms of the additives being responsible for the inhibition of scaling. By variations of both the composition and the concentrations it is demonstrated that a combination of ethylenediamine tetra(methylene phosphonic acid) and diethylenetriamine penta(methylene phosphonic acid) is the most suitable basis for the development of a tailor-made formulation. Additional properties like the fulfilment of particular dispersion requirements are realised by a partial exchange of the phosphonates against other additives (other phosphonates or polymers) without a drop in the hardness stabilisation performance. The examples show that the development of a real synergistic combination can be accomplished by a screening approach and that phosphonic acids are really essential to preventing scaling.

The "Qualification of Different Test Stains in Detergent Examination" was investigated by *T. Hilgers* (together with *Anke Ophüls* and *J. Bohnen*), wfk Research Institute for Cleaning Technology e.V., Krefeld, Germany. A wide range of methodic approaches and actual test methods are used worldwide for testing the performance of laundry detergents. Principally, all methods need washing machines, detergents, laundry, soil ballast (e.g. SBL2004) and tracer stains. It has been discussed occasionally whether uniformly stained standard tracer stains are 'artificial' (i.e. not 'natural'). However, manually prepared or other round stains are no natural stains either – all stain systems are models supposed to represent aspects of reality.

Uniformly stained tracer stains were developed to improve reproducibility. A few existing stains are additionally heat treated or represent combinations of several stain substances ('effect stains'). All tests are supposed to provide performance results reflecting (consumer) reality; suitability of any of the model systems depends solely on their ability to provide results for reliable performance assessment.

Laboratory tests differ from the wide range of possible consumer reality in several aspects (Table 3).

Most uniformly soiled tracer stains use stain substances that are also used for round stains, e.g. wine, coffee, tea, berry juices, oils, fats, etc. Uniformly soiled tracer stains were developed to improve reproducibility, not to change stain characteristics. The vast majority of standard stains (at least from wfk) are prepared fresh without high temperatures or any other special treatment.

Extensive comparative tests using different stain systems confirmed that preparation of small batches using different fabric substrates, finish and pre-treatment is beneficial for testing, e.g. soil release polymer performance. Apart from that, uniformly soiled standard stains in general showed better reproducibility while providing comparable performance results. It could be confirmed that standard stains are a good solution for addressing issues with dissatisfactory reproducibility.

An "Assessment of Color Damage Caused by Bleach Systems" was presented by *Hauke Rohwer* (co-author: *T. Wieprecht*), Ciba Spezialitätenchemie GmbH, Grenzach-Wyhlen, Germany. Bleach, one of the primary wash effects of modern laundry detergents, aims to decolorize natural chromophores like tea, coffee, chocolate or red wine that can cause severe staining on textiles. It is an inherent problem of bleach that artificial dyes as used for textile dyeing can suffer damage from detergent bleach systems as well.

Recently, a set of 40 different textile dyes for color safety tests was developed by *D. Phillips* together with detergent manufacturers (A.I.S.E. dye set). This set represents a broad range of different dyes in the market. It is hence an appropriate tool to get a first impression on the general dye safety of bleach systems on a large variety of chemically diverse dyes. However, since the exact nature of the dyes and their market relevance is currently not published it is not straight forward to conclude from tests with the A.I.S.E dye set to the situation in practice.

Therefore, a set of 30 cotton dyes (MRD Set) was introduced. The dyes of the MRD set were selected to represent closely the textile dyes on the market. The design principles as the used textile substrate, colors and dye classes were discussed. The color index (C.I.) numbers of the individual dyes are disclosed. The dye damage of the percarbonate/

Reality	Tracer stain
Wide range of fabric substrates	selection
Wide range of possible finish	selection
Wide range of possible stain substances	selection
Wide range of actual stain 'application'	selection
High temperatures unlikely	optional
Combination stains unlikely	optional

Table 3 Laboratory tests and consumer reality (*source: T. Hilgers*, wfk)

	TAED	Mn Cat1	Mn Cat2
A.I.S.E.-Set	4.4	3.9	2.6
MRD-Set	2.2	2.0	1.6

Table 4 Average ΔE values of color changes (*source: Hauke Rohwer*, Ciba)

TAED (tetraacetylethylendiamine) system and that of two percarbonate/bleach catalyst systems were compared on the new as well as on the A.I.S.E. dye set. The results in Table 4 are given as the average ΔE value (change in color) for each set after 8 washes.

Both dye sets result in similar conclusions on the general dye safety of the respective bleach systems. While looking at the damage of single dyes (not given here) the MRD set provides in addition the opportunity for a more detailed insight with respect to the market relevance of the dyes. Since it is not envisaged to establish a second dye set for bleach damage testing, the A.I.S.E. dye set will probably be extended with 4 dyes of the MRD set in order to improve the market relevance of dye chemistry as represented by the A.I.S.E. set.

Innovations: Turning 70% Flops into 70% Tops

Innovation is the main driver for lasting added value oriented growth. *W. Twardawa*, GfK Panel Services Germany, Nuremberg, analysed the "Bermuda Triangle of Innovation – 70% Flops – An Avoidable Waste of Resources". For every second company innovation is indispensable. In Germany about 6,500 products are launched annually in the categories detergents, toiletries and hygiene products, this means 130 per week! Looking at all active products in these categories, 28% are younger than 18 months (comparison: fast moving consumer goods without fresh food: 23%). The categories heavy duty detergents and machine dishwashing are leading with 40% and 39%, respectively.

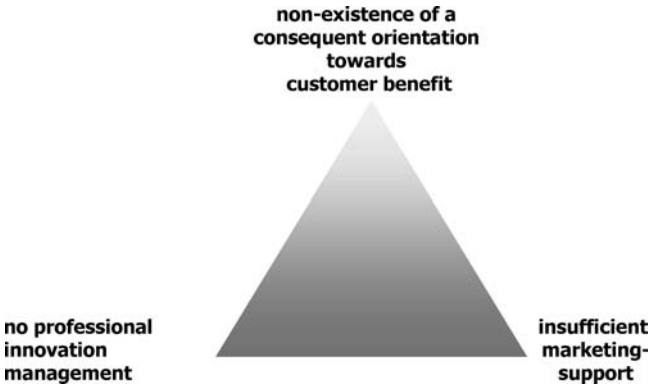

Figure 18 The Bermuda triangle of innovation (*picture credit: W. Twardawa*, GfK)

Nevertheless, 70% of all new products are not listed anymore after 12 months. This equals a misinvestment of 1 billion euros per year. Reasons for this are the non-existence of a consequent orientation towards customer benefit, no professional innovation management and insufficient marketing-support (Fig. 18).

More than one third of all household desire more product innovation, thus potential exists. The desire for real performance- and quality-improvements is heading the list (75%) followed by the request for more convenience (35%) and health/wellness-oriented innovations (22%), as an innovation research study of Roland Berger and GfK shows.

From a market perspective, the key success factor of innovation lies in the appreciation of the product by the consumer. 12 months after product launch the market penetration should represent at least 5% and the repurchase rate 30% (Fig. 19). Only 16% of all innovations are runners right from the start, 60% of all flops are failing due to a poor concept and 40% due to a wrong implementation. The producing industry expects that 17% of new products should have a low, 56% a medium and 27% a high degree of innovation from a consumer's point of view. GfK research based on the years 2003 until 2005 shows another picture: in fact, 53% of all new products have a low, 30% a medium and only 17% a high degree of innovation. New products with a high or medium degree of innovation have twice the chance to be more successful than other, losers fail due to a too low degree of innovation.

In addition, the price-performance ratio of innovations is not always coherent. Two thirds of all flops fail due to an over-promising price. Highly important is the consideration of an umbrella brand strategy. 88% of all innovations are launched under an umbrella brand, from which two thirds are premium brands. A launch under an umbrella brand is about 30% more efficient, but the innovation must fit the brand essence of the umbrella brand and its price-performance ratio. A premium umbrella brand only is not enough, the innovation needs a clear USP to justify a premium price and therefore the launch under the umbrella brand. The stronger and the more trustworthy an umbrella brand, the higher the risk of damaging its image with a flop and – vice versa a weaker umbrella brand highly profits from a strong innovation.

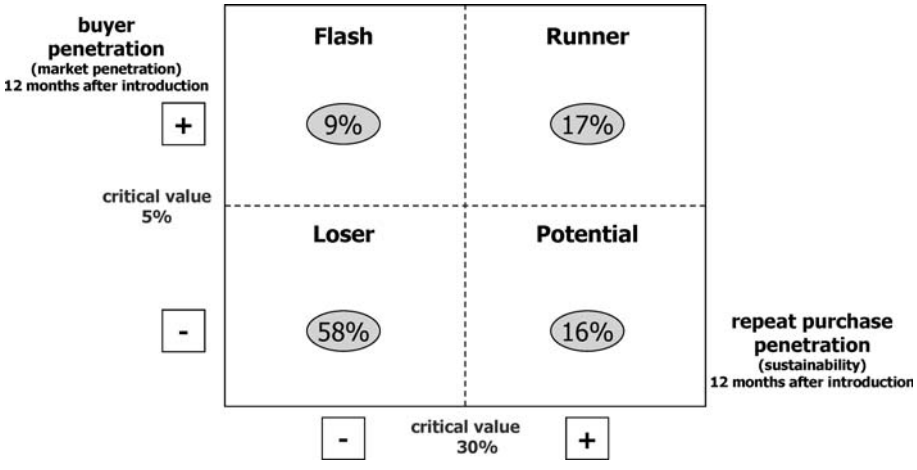

Figure 19 The key success factor of innovation lies in the appreciation of the product by the consumer (*picture credit: W. Twardawa*, GfK)

As per DIW, Germany has enough innovations and is even No 1 in terms of technological innovations. However, there are only not enough innovations that are well brought to market or in line with the market needs. If we succeed to turn 70% Flops into 70% Tops, the launch efficiency will increase by about 1 billion euros per year. The Bermuda Triangle of Innovations can be circumnavigated with right positioning, consequent implementation and lasting marketing-support.

Sustainability and Environmental Evaluation of Detergents

"The Path from Biodegradability to Sustainability – Is a Change of Paradigm Due?" asked *F. R. Schröder,* Henkel KGaA. In the late 1950's and early 1960's the detergent industry was challenged by society due to the foam visible on rivers and canals. Very soon the industry accepted this challenge and started to develop methods to cope with this issue. Later, with the availability of ecotoxicological data, the concept of environmental risk assessment was introduced. This concept is based on a comparison of the predicted environmental concentration (PEC) and ecotoxicological no-effect concentration (PNEC) of a substance. The various environmental labels that are propagated by competent authorities and NGOs (e.g. 'Blauer Engel', Nordic Swan, and the European Eco-flower) aim at the improvement of the ecological risk by minimising the ratio between PEC and PNEC. Hence, the ecotoxicological properties of the substance were the major matter of concern. Meanwhile, the industry initiated the A.I.S.E. Code of Good Environmental Practice. This programme aimed at reducing the amount of the detergent used, of poorly biodegradable organics (PBO), and of packaging material by 10% each. All these initiatives focus very much on the product as such. In order to further optimise the overall sustainability it is of key importance to check all processes. Life Cycle Analysis studies reveal that the use phase (i.e. the washing cycle) is the most energy consuming step in the overall process. Hence, improving the performance of detergents to lower washing temperature may be one way to save energy and reduce the environmental burden. Moreover, it has to be taken into account that sustainability comprises not only environmental but social and economic factors as well. The A.I.S.E. initiated in 2004 the A.I.S.E. 'Charter for Sustainable Cleaning' as an overall initiative to improve the sustainability profile of this industry (www.sustainable-cleaning.com). Companies that have successfully passed the entrance check are entitled to bear the Charter logo (Fig. 20).

The progress achieved will be recorded using ten Key Performance Indicators (KPIs). A.I.S.E. includes this information in its annual Sustainability Report. With the concept of sustainability further enhancement potentials in environmental and consumer protection should be developed. Transparency and intense communication are in the focus of all activities.

"The Use of Life Cycle Assessment and Other Tools in a Consumer Goods Company on Its Way to Increased Sustainability" was analysed by *D. Schowanek*[1] (together with *Rana Pant*[1], *J. Dewaele*[1] and *Marina Franke*[2]), [1]Procter & Gamble Eurocor, Strombeek-Bever, Belgium, and [2]Procter & Gamble Service GmbH, Schwalbach, Germany. The development of innovative products in Procter & Gamble is driven by a comprehensive understanding of consumer needs, a commitment to deliver performance and value, as well as a constantly improving sustainability profile. This is the concept of '*consumer-driven sustainable brand innovation*'. The Lecture discussed the use of Life Cycle Assessment (LCA) and the Product Sustainability Assessment Tool (PSAT) in fostering a culture of sustainable brand innovation within P&G.

Figure 20 Logo of the A.I.S.E. 'Charter Sustainable Cleaning' (*picture credit: R. Schröder*, Henkel)

LCA has become a key tool for the technical assessment as well as the internal and external communication of environmental trends in product development. Two LCA cases were discussed: one on cold washing household detergents in France (Ariel Actif à froid), and one on kitchen surface cleaning wipes. The Ariel Actif à froid case study allows to illustrate the broad environmental benefit of washing at colder temperatures, as well as the cost saving that can be realized by the consumer. The second study illustrates that the use of household wipes for kitchen surface cleaning is associated with a very different environmental fingerprint than using either spray or all-purpose cleaner products. None of the 3 options stands out as overall environmentally preferable over the other. Both case studies illustrate that for consumer products the use phase often plays a dominant role regarding environmental burdens over the entire life cycle. In collaboration with the consumer some of the more substantial environmental gains can be realised. A thorough knowledge of consumer needs and habits & practices is a prerequisite for creating win-win solutions. P&G believes that consumer-driven innovation not only improves product performance but may also positively impact the environmental profile.

Next to LCA and environmental risk assessment tools were also investigated and developed to address all three dimensions of sustainability, i.e., environmental protection, social responsibility and economic development. Designed by P&G experts, the Product Sustainability Assessment Tool (PSAT) is an exploratory tool to evaluate the integration into P&G's products of the three pillars of sustainable development. PSAT facilitates the analysis and identification of the external strengths and weaknesses of specific products in a sustainability context. PSAT assessments cover information about manufacturing sites, supply chain management, environmental protection, social responsibility, etc. PSAT follows a semi-quantitative approach, based on a questionnaire that captures information from R&D, Product Safety, Human Resources, Finance and Marketing departments. More information on this approach to environmental and sustainability assessments can be found respectively at www.scienceinthebox.com and www.pg.com/company/our commitment/sustainability

R. Stamminger[1] (co-author: *Gisela Goerdeler*[2]), [1]University of Bonn and [2]Deutscher Hausfrauenbund, Bonn, Germany, presented the "Sustainable Washing Day – What's the Con-

sumers' Role?". Data about the behaviour of the consumers when laundry washing were recorded in the context of the 'Action day for sustainable washing' via a consumer inquiry and via the 'wash computer' (www.aktionstag-nachhaltiges-waschen.de). These data show that despite a generally high satisfaction with the received wash results, nevertheless many problems remain for the consumers. These are solved in different ways or simply ignored. Concerning the sustainability of this behaviour the inquiry shows improvement potential points in many places. For example, 37% of the consumers quote to wash the laundry again, when discontent with the wash result achieved. Another critical point seen is the habit, particularly in younger households, to have just one kind of detergent in the house. On the other hand the recorded wash temperatures show that already many consumers adapted their program selection to the improved abilities of modern detergents and washing machines in the low temperature range. Future activities should therefore address those consumer groups, which did not discover these positive developments yet for themselves as meaningful. It remains reserving the further discussions in the Forum Washing, to pull from it the necessary consequences.

The "Use of the EU Ecolabelling DID List to Evaluate Products" was analysed by *L. Nitschke*[1] (together with *I. Malcomber*[2], *P. Masscheleyn*[3] and *J. Steber*[4]), [1]Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit, Munich, [2]Unilever, Sharnbrook, U.K., [3]Procter & Gamble Eurocor, and [4]Henkel KGaA. The consideration of the environmental properties of formulated products intentionally going to the drain (e.g, detergents, shampoos) is a general standard in products comparisons, for instance, by consumer magazines. The parameter 'critical dilution volume' (CDV) previously developed for the EU Ecolabel of detergents proved to be a suitable descriptor for such comparative environmental evaluations. The CDV takes account of the proportion and the basic ecological properties (biodegradation/elimination, aquatic toxicity) of all product ingredients, thus, easily enabling a ranking of formulated products according to fundamental criteria for environmental evaluation.

The Detergents Ingredients Database (DID) list of the EU Ecolabel represents a public and scientifically founded information basis for such environmental data of product ingredients. Recently (2004), the hitherto used DID list (first publication in 1995) was reviewed and enlarged in terms of new substances and data. However, also the rules for calculation of the CDV-relevant descriptors of biodegradability/elimination and aquatic toxicity have been altered. In many cases, these changes result in an unrealistic description of the environmental effects and fate of product ingredients and ultimately lead to scientifically untenable conclusions regarding the ecological evaluation of the formulated products. The results of an expert group recruited from members of the Hauptausschuss Detergentien (HAD) have been presented providing a revised DID list. This revised list is based on the updated, publicly available substance information from the new EU Ecolabel DID list, but takes the rules into account applied for derivation of CDV-relevant environmental descriptors according to the previous DID List (1995). The comparison of products based on the current DID list (2004) and the revised DID list, respectively, shows that the application of the latter is a prerequisite for a realistic and consistent environmental product ranking.

The theme of *M. Bernhard* (together with *Jutta Müller* and *T. P. Knepper*), Europa University of Applied Sciences Fresenius, Idstein, Germany, was "Biodegradation of Linear Alkylbenzenesulfonates and Sulfophenylcarboxylates in Wastewater – Comparison of an Optimised Lab-scale Membrane Bioreactor with an Activated Sludge Treatment". Linear alkylbenzenesulfonates (LAS) are anionic surfactants, which are used in the formulation of laundry powders, as rinsing agents and household cleaning agents. They are used in large amounts, 2.2 million tons per annum, and via sewers they are transported to wastewater treatment plants (WWTPs) after use (6). Their primary degradation is excellent, up to 99% will be removed, mainly by biodegradation. But their degradation products, sulfophenylcarboxylates (SPC), formed after aerobic biodegradation of LAS, are found in wastewaters and surface waters (6).

In order to study the biodegradation of LAS and SPC during wastewater treatment by comparing a lab-scale membrane bioreactor (MBR) running in parallel to activated sludge treatment (AST), the analysis of both LAS and SPC is needful to calculate and compare their removal. This was performed during a monitoring campaign beginning July 2004 and ending March 2005 at the WWTP Wiesbaden, Germany, where an MBR was installed. The influent and effluent samples of WWTP and MBR were analysed by liquid chromatography/mass spectrometry following solid phase extraction. Compared to the AST, the MBR showed significantly better removal for the investigated poorly biodegradable SPC (7). This can be explained by an increased sludge retention time. An application of such an optimised MBR may lead to a reduction of these compounds in the watercycle.

"What Is the Benefit of a Total Dispensation of Phosphates in Detergents and Cleaners for the Environment?" asked *T. Wind*, Henkel KGaA. The new EU Detergent Regulation (EEC 648/2004) requires the Commission to evaluate the use of phosphorus in detergents by April 2007. When justified, a legislative proposal for a step-wise phase out or a restriction to specific applications may result from this process. It has been well known for a long time that elevated levels of phosphate in surface water may lead to eutrophication of the aquatic environment. Therefore, legislative actions were introduced during the past decades, e.g. the implementation of the Urban Waste Water Treatment Directive (91/271/EEC) or legislative and/or voluntary P restrictions from detergents in some countries. The Lecture provided a general overview of a gross source-apportionment for phosphorous in 18 European countries of human wastes, detergent use, industrial, diffuse and natural sources.

Because the detergent industry currently lack appropriate alternatives to phosphate in automated dishwashing detergents (ADD) focus is given to their environmental impact and the paper asks the question of the significance and effectiveness of possible future P reduction measures of detergents. Scenarios reflecting the current wastewater treatment situation and future 'what if' scenarios of P in surface waters are shown for three exemplary EU member states (Germany, Belgium, and Portugal). The analysis indicated the major input of phosphorous are diffuse sources and human wastes. However, phosphorus from the uses of detergents may account for up to 28% of the total P in the environment, where sewage treatment situation is bad and P-based laundry detergents are widely used (e.g. Portugal). As result from the analysis it can be concluded that P from the use of ADD accounts for only 1 to 6% of the total P in the environment today (depending on the country). This fraction can be further reduced to a maximum of <1 to 4% of the total P in surface water if a sewage treatment situation as envisaged by the UWWTD is successfully reached. The most significant reductions, however, can be achieved in countries where P-containing laundry detergents are not

yet replaced on the market and by introducing P-free product alternatives for laundry detergents. It can be concluded that ADD as P source may not significantly contribute to the nutrient status of surface waters, especially in eutrophication sensitive areas, where efficient P removal from sewages is regulated by the UWWTD.

European Detergents Conference 2007

Please mark your calendar for the

3rd European Detergents Conference which will be embedded in the 54th SEPAWA Congress: October 10–12, 2007, Congress Centrum Würzburg.

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