FIRST EUROPEAN DETERGENTS CONFERENCE REPORT

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The First European Detergents Conference – Embedded in the 52nd SEPAWA Congress

The First European Detergents Conference embedded in the 52nd SEPAWA Congress took place in Würzburg from October 12th to 13th, 2005. More than 1200 attendees came to this fine baroque city and were given value in 25 lectures in the field of *Raw Materials for Detergents, Cleaners and Washing Aids, Basics of Detergency and Rheology* as well as *Product Safety, Hygienic Aspects and European Legislation*, and *Market Situation*. Moreover, in the SEPAWA Sections on *Cosmetics* also some surfactant-related topics were presented.

The complete program contained 40 lectures and an extensive poster exhibition. Keynote speaker was Professor H.-J. Bullinger, President of the Fraunhofer Society, Munich, who held an impressive lecture on “The Feat of Innovation – Perspectives of Future Markets and Work”.

To initiate the European Detergents Conference the SEPAWA Congress was organised jointly with the Expert Group of Detergent Chemistry of the Society of German Chemists (GDCh) for the first time. After the opening address of Dr. Lothar Rasthofer, First Presiding Chairman of the SEPAWA, Dr. D. Schermer, Presiding Chairman of the Expert Group Detergent Chemistry (GDCh), emphasised in a special welcoming address to the First European Detergents Conference (EDC) that the EDC brought to life for the first time is intended to bring together specialists from academia, public authorities and the industry as well as other interested groups on a more general European level.

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Almost the whole spectrum of detergent ingredients was addressed: dynamic surfactants and surface-active agents with natural structural motifs, detergent polymers and dispersants,

bleaches, chelating agents and colorants. This year the polymer theme run like a thread through the program. Additionally, an evaluation of textile piling and the application of liposomes as part of a wellness concept were presented. The surfactant-related lectures held in the Cosmetics Section of the Congress are also reported here.

Dynamic and Mild Surfactants, Surfactants from Nature

Industrial processes become faster and faster. The corresponding formulations have to keep pace with new technical solutions like the replacement of isopropanol in fountain solutions for off-set printing or spray coating in paper production. In this context, J. G. Tropsch (co-authors: R. Böhn, S. Hess and G. Oetter), BASF AG, Ludwigshafen, Germany, recommended “Highly Dynamic Surfactant Systems – New Formulation Concepts”. Fast diffusion of surfactants to interfaces and the formation of interfacial films to lower the interfacial energy are the fundamental molecular mechanisms which have to be optimised for all high speed spraying and wetting processes. Knowledge about structure/property relationships is the key requirement for the development of new dynamic systems.

Surfactants based on a C₁₀ Guerbet alcohol, able to reduce the interfacial tension within milliseconds, can improve the performance of formulations for spray, wetting and cleaning applications. By moving from a pure ethoxylate to an alkoxylate the critical micelle concentration (cmc) can be further reduced while keeping the dynamics of the surfactants at the same level. These alkoxylated surfactants unexpectedly show an emulsification capability similar to the one of longer alkyl chain surfactants. The C₁₀ Guerbet alcohol surfactants can further be used as basis for synergistic surfactant mixtures with high dynamics and low cmc. With

these formulation concepts the application range of standard surfactants can be extended [1].

In the last few years the interest in highly specialised synthetic surfactants incorporating natural structural motifs has increased remarkably. D. Blunk¹ (co-authors: P. Bierganns¹, N. Bongartz¹, Renate Tessoroff¹ and Cosima Stubenrauch²), ¹University of Cologne, Germany, and ²Department of Chemical and Biochemical Engineering, UCD, Belfield, Dublin, Ireland, presented “New Surfactants Made of Natural Compounds”. The variety of naturally occurring structures used as parts of such ‘designer surfactants’ ranges from simple amino acids and short peptides over carbohydrates to steroids. Surely, one of the most prominent examples in this respect and probably the breakthrough for tailor-made surfactants in highly specialised applications was the use of a surfactant structurally similar to membrane lipids for the first successful crystallisation of a membrane protein, which finally led to the award of the Nobel Prize in Chemistry 1988 to R. Huber, H. Michel and J. Deisenhofer. Other important applications of surfactants are the employment of their lyotropic liquid crystalline phases as templates for polymerisation or precipitation, their ability to accelerate the transport of genetic material through biological membranes or even their use as novel reaction media. A number of new promising nonionic amphiphiles such as myo-inositol monoethers and -esters as well as diethers, and phosphine oxides containing hydrophobic side chains derived from citronellol or higher terpenoids have been introduced. The investigation of their surface activity and detergency is ongoing work.

A. Behler (co-author: Iris Hütter), Cognis Deutschland, presented “Laur-eth-7 Citrate – The ‘Vitamin’ of Surfactants”. Following the continuous trend towards added value ingredients Cognis Care Chemicals presented Planta-

pon® LC 7 (INCI: Laureth-7 Citrate). Based on citric acid this advanced care surfactant uniquely combines the benefits of moisturizing fruit acids with a degree of mildness that far surpasses that of traditional mild surfactants.

Several compatibility studies proved the exceptional mildness of Laureth-7 Citrate while still showing the characteristic moisturizing qualities of natural fruit acids, even under rinse-off conditions. Beyond that regeneration and re-vitalization effects can be achieved just as good as excellent sensorial behavior on skin and hair.

Surfactant formulations containing this novel care additive moreover show decisive advantages over conventional

systems in terms of hair conditioning, particularly hair feel and mildness (Fig. 1), moisture (Fig. 2), and conditioning to cosmetic cleansing formulations, such as hair and body shampoos, baby and facial washes as well as shower/bath oils.

K. Booten, Orafit, Tienen, Belgium, gave an overview on "Polymeric Carbohydrate-based Surfactants and Their Use in Personal Care Applications". Polymeric carbohydrate-based surfactants, especially inulin-based surfactants, are a new generation of surfactants that can be used at extremely low use levels to stabilise emulsions and dispersions.

Because of the absence of these materials in the aqueous phase of an

emulsion, the skin feel will always be light and non-sticky. Inulin-based surfactants such as INUTEK® SP1 (INCI: Inulin Lauryl Carbamate – ILC) will not contribute to any viscosity of the continuous phase and so, even emulsions containing high loads of oils will stay highly fluid. The tolerance towards the presence of electrolytes is remarkable and unique; inulin-based surfactants will not be salted out from the interphase.

Compared to most other emulsifiers and surfactants, this new class of materials show no skin neither eye irritation, has no acute toxicity, is completely biodegradable and non-aquatic toxic. In personal care formulations, a wide range of possibilities are opened, for instance, high-loaded oil emulsions with light skin-feel, sprayable sunscreens, high-silicon-in-water emulsions and foundations.

Bleaches, Colorants, and Complexing Agents

The new European Detergent Regulation came into force on October 8th, 2005, dealing with the aerobic biodegradation of surfactants so far. An extension of the Regulation as to all main organic detergent ingredients and anaerobic biodegradation aspects shall be reviewed until April 2009. In this context, L. Cuypers (co-authors: Martina Hirschen and G. Reinhardt), Clariant Deutschland GmbH, Frankfurt/Main, Germany, discussed "Bleaching Product Development in View of Ecological Aspects".

Within the scope of the extension of the Regulation also bleach activators will be affected, whereat in the authors' opinion thought should been given to a specific characteristic of this ingredients category: Whereas other detergent ingredients like surfactants, builders or solvents act in the washing process due to physical effects and therefore arrive at the environment in a chemically unchanged way, bleach activators react with peroxo compounds during the washing process and hence change their chemical structure. So, regarding bleach activators, the environmentally relevant compound differs from the compound being existent in the washing agent.

The nitrile quat cyanomethyltrimethylammonium methylsulfate for example has to be classified as not readily biodegradable. Studies of the kinetics of the reaction of this compound with hydrogen peroxide at pH 10 show that the nitrile quat is converted com-

Laureth-7 Citrate Exceptional mildness

Figure 1 Laureth-7 Citrate: exceptional mildness (Source: Iris Hütter, cognis)

Laureth-7 Citrate Increased moisture retention

Figure 2 Laureth-7 Citrate: increased moisture retention (Source: Iris Hütter, cognis)

pletely to the corresponding amide and betaine even at 20 °C within a few minutes. Thus, using the nitrile quat in heavy-duty detergents, only the amide and betaine would be released into the environment. Because both these compounds are readily biodegradable (Fig. 3), the poor biodegradation of the starting nitrile quat should not lead to a ban on this bleach activator in the authors' opinion.

In recent years, PAP, a revolutionary bleaching agent and active for disinfecting preparations, has been introduced to the detergent industry. *R. Garaffa* (together with *U. Bianchi*), Solvay Chimica Bussi, Italy, recommended "Formulating PAP (Phthalimido-peroxy-hexanoic Acid) in Detergent Compositions for Consumers or Industrial and Institutional Applications". The solid phase, crystalline nature of PAP proved recently offers additional advantages to the formulator in terms of flexibility of their product design and in view of different application targets. Such a crystalline form will be useful to formulate PAP both into powder detergent compositions and into water-based, liquid compositions. Consequently, the outstanding physical-chemical stability of PAP crystals will be retained, thus offering to those compositions a prolonged shelf-life, stability and safety. On the very application, quick solubilisation of PAP crystals will be possible when their size was designed in the preferred range of particle size distribution. On the contrary, controlled release of PAP in the washing bath will be delivered by the selection of particle sizes toward coar-

ser values, with potential benefits in terms of performance of detergent compositions designed with other ingredients having poor compatibility with peroxygen such as enzymes.

"Perspectives of Chelating Agents in Cleaning Applications" were discussed by *K. Baldenius* (together with *M. Hartmann* and *L. Kissau*), BASF AG. Industry's search for eco-friendly aminocarboxylate chelating agents has resulted in a few new products. Among these, methylglycine diacetate (MGDA) has turned out to be the ultimate fit to the demand of the detergent and cleaning industry. MGDA combines strong binding to metal ions with a low molecular weight (= high efficiency). In contrast to other strong chelating agents like glutamic acid diacetate (GLDA) and aspartic acid diacetate (ASDA) MGDA (Fig. 4) is readily biodegradable and very safe to use. There is no hazard labeling required for MGDA containing products in the EU. After the finalisation of a long term, chronic carcinogenicity study in rats, MGDA can be ranked among the three most thoroughly tested aminocarboxylates. This profile opens new avenues for uses in household applications, in particular surface cleaning, dishwashing and laundry.

Color labels products and product qualities and therefore delivers an argument to buy something. It helps to remember a product and as a new trendy effect to introduce novel creations into the market. *H. Bellaire*, BASF AG, focused on "The Power of Color and Its Application in Detergents and Cleaners". In the detergent

industry washing powders and laundry tabs, fabric softeners, hand and automatic dishwashing detergents, liquid cleaners, toilet bowls and gels as well as soap are frequently colored.

Suitable colorants are pigments, powder or liquid pigment preparations (for laundry powders or tabs) or soluble dyes (for liquid cleaners). For soap only colorants should be used that are proven for cosmetics, for hand dishwashing detergents only colorants proven for the contact with food.

The stability of colorants over a wide range of pH, against oxidative and reductive media as well as light-fastness are important. Furthermore, an unwanted dying of garments or hard surfaces to be cleaned should be avoided. The usual light protection agents are not suitable to guarantee the light-fastness of dyes in liquid cleaners. Instead of that the packaging must include UV absorbers. Metal complex colorants offer a new solution to apply colorants with a high grade of light-fastness in aqueous systems. Thus, with castor oil ethoxylates it is readily possible to manufacture a suspension, which can be simply mixed into aqueous systems and delivers completely transparent colorings.

Detergent Polymers

"Amphoteric Polymers for Cleaner Applications" were presented by *Heike Becker*, BASF AG. Modern cleaners not only promise effective dirt removal and a fresh smell; cleaning today has to be easy, fast and long-lasting.

For this purpose a special amphoteric polymer, Sokalan® HP 70, has been developed. A careful balance of charges together with the choice of structure have been the key to the successful design of this modified polyamine. It can be used in cleaner applications or other processes, where hydrophilisation of surfaces is required.

As the surrounding pH value changes the charge density of the polymer, Sokalan® HP 70, exhibits its highest adsorption and best application results in acidic to neutral formulations, as utilised in bathroom cleaners. When applied to glass, ceramic or metal, the polymer leads to a hydrophilic modification of the surface. Application tests like contact angle measurements (Fig. 5) and microscopic investigations have shown that Sokalan® HP 70 is not directly washed off by following rinse cycles. If the polymer is used in

Figure 3 Biodegradation of cyanomethyltrimethylammonium methylsulfate (nitrile quat), carbamoylmethyltrimethylammonium methylsulfate (amide) and betaine (DOC die away test)
(Source: L. Cuypers, Clariant)

The Feat of Innovation – Signposts to Tomorrow's Markets and Work

Keynote address by Prof. Dr.-Ing. habil. Hans-Jörg Bullinger, President of the Fraunhofer-Gesellschaft, Munich

Global competition has increased in both scope and intensity over the past few years. Knowledge and markets have become international; everyone in the 'global village' is everyone else's neighbour, rival – and customer, too. Risks and opportunities have grown in equal measure, and the time that elapses between an entrepreneurial initiative and its consequences has grown shorter.

In economic terms, this means that a company's business results will immediately reveal how well it has adjusted to the changes in the market. Companies that fail to adapt quickly enough will be left behind. Only those who are significantly faster or better than all the others can achieve real growth; only companies that have created a vital culture of innovation can hold out against the unceasing challenge.

The Fraunhofer-Gesellschaft undertakes applied research aimed at promoting the innovative capacity of German industry and thus strengthening Germany's status as an industrial location. Our work involves analysing markets, developing new products, processes and services, and enhancing existing production plant and organisational structures. We play our part in ensuring that German companies are able to gain a competitive edge in the face of international competition, and can maintain and expand that edge.

To help us find our bearings in the fast-moving current of technological trends around the world, our experts have evaluated numerous foresight studies conducted by other industrial nations and roadmaps drawn up by international corporations, and have discussed and further evolved the results with internal and external experts. A comparison of national and international research trends with the present competencies and strengths of the Fraunhofer-Gesellschaft has revealed twelve areas of technology in which we

particularly expect to see market-relevant innovations.

These twelve thematic areas have now been collected under the title of 'Signposts to tomorrow's markets'. They are characterised by their outstanding potential for innovation and their remarkable relevance to the market. The Fraunhofer-Gesellschaft is particularly well equipped to meet the great need for research and development in these areas. The Fraunhofer Institutes have therefore joined forces with partners from industry and are vigorously pressing ahead with the corresponding activities.

By purposefully concentrating our research and development activities in this way, we will be strengthening German industry as a provider of innovative products, processes and services that are successful all over the world. We will be tapping new markets and achieving sustainable growth as well as new work, and ultimately only this can generate revenues that will fill our coffers once more. If we manage to secure a share in the growth markets, we will be making an important contribution to Germany's future as an industrial location. The 'Signposts to tomorrow's markets' will give us our bearings on the way to this important goal.

The 12 signposts of tomorrow's markets are as follows:

1. Internet of things: Parcels that deliver themselves

The Internet is a self-organising distribution system. If the same principles are applied to real merchandise, each parcel can find its own way to the customer.

2. Smart products and environments: Invisible helpers at the ready

Electronics create a helping environment: Sensors and microchips locate devices, control service robots, remind us of important things to do and relieve us of burdensome tasks.

3. Micro power engineering: Mobile power supplies

Mobile electronic devices such as cell phones and digital cameras have become an essential ingredient in our lives: Miniaturised fuel cells will keep them powered up for longer.

4. Adaptronics: Self-regulating structures

Adaptronic systems actively dampen vibrations: Machines and cars run quietly when noise is cut down or shut out.

5. Simulated reality: Materials, products, processes: Future worlds inside a computer

The gap is closing between ideas and reality: Modern simulation methods allow the properties of components and other products to be tested as early as the design stage.

6. Human-machine interaction: An end to button pushing

Interaction between people and machines is growing easier and more intuitive. Design engineers and planners can move around in virtual reality systems without the distraction of complicated input devices.

7. Grid computing: Link up wherever you like

People are more productive when they co-operate – and the same applies to computers. Standard PCs linked together to form a grid are even capable of outperforming supercomputers.

8. Integrated lightweight construction systems: Weight-loss diet for four-wheel patients

Lightweight construction methods bring immense benefits to vehicle manufacturing: When less mass needs to be moved, energy consumption is reduced accordingly.

9. White biotechnology: Nature's own chemical plant

Plants produce useful raw materials: Through genetic engineering, algae and higher forms of plant life can be encouraged to manufacture valuable drugs and chemicals of remarkably high quality.

10. Tailored light: Using light as a tool

The laser is steadily being adopted for many new industrial applications. The use of special mirrors to guide the beam with great precision speeds up the welding of complex parts and optimises the manufacturing process.

11. Polytronics: Printed circuits – luminescent wallpaper

Conductive and luminescent polymers are creating new perspectives for the design of innovative products such as low-cost electronic labels, roll-up displays and smart clothing with integrated sensors.

12. Security: The reassuring face of high tech

Many security technologies are based on unique attributes that allow a person to be identified. Biometric methods have proven to be a highly reliable solution.

shower cleaners, the effects last for several days.

The water forms thin films on the modified surface instead of drops and this rinse behavior leads to reduced drying times (Table 1). Furthermore, typical watermarks of hardness salts, which can crystallise in the drying drops, are avoided and, thus after drying, the surfaces remain shiny and

clean. In addition to avoiding watermarks, lime soap (formed from soap and water hardness) which usually leads to stubborn stains, is also easily rinsed off from modified surfaces. In conclusion, Sokalan[®] HP 70 helps to keep the bathroom clean and sparkling without daily cleaning.

S. Jaynes¹ (co-authors: E. Martin² and G. Merkle²), CIBA Specialty Che-

micals, ¹Tarrytown, NY/USA, and ²Grenzach, Germany, recommended "Polymers for Household Application". A range of highly efficient acrylic polymers for household applications has been introduced. The products consist of three anionic and three cationic polymers covering most home and fabric care applications. In addition, a range of new polymers for surface

Figure 4 Strong and weak chelating agents (Source: K. Baldenius, BASF)

modification and other performance benefits is also being developed.

The anionic thickeners are especially suitable for the formulation of transparent liquid detergents. They are compatible with anionic and nonionic surfactants and show highest efficiency from pH = 7 to pH = 12. Associating hydrophobic side groups are present in two polymers. They improve the electrolyte tolerance and enable thickening at higher pH and surfactant

concentration (Fig. 6). In general, the non-associative polymer is most suitable for mild formulations with low electrolyte content.

The cationic polymers are composed of two liquid rheology modifiers and one solid-grade polymer. The solid-grade polymer is commercially available in a bead form. These cationic polyelectrolytes exhibit excellent compatibility with nonionic and cationic surfactants in acid formulations. Both

liquid dispersion polymers are best suited for fabric softener applications, increasing the viscosity at low dosage and providing a creamy appearance to the formulation. The solid-grade polymer has been especially developed for transparent acid hard surface cleaners, but is also suitable for fabric rinse conditioners.

A new range of polymers is also being developed to deliver unique performance benefits in various household applications. These include novel cationic polymers designed to give tailored interactions with surfaces, providing easier cleaning and other consumer desirable benefits.

In the past, there have been many innovative developments in the field of household detergents, both in terms of forms and formulations. Laundry detergents were traditionally manufactured as physically mixed powders, pastes or solutions. The dry form has evolved through low-density spray-dried powders to compact high-density blends to tablets. There have also been developments in terms of the ingredients employed. Powders have evolved from simple leach-alkali mixes through various complexities of surfactant-builder blends based on initially soluble silicates, then polyphosphates, later zeolites, and more recently carbonate and carbonate/citrate builders. In "Adapting Dispersant Polymers to the Changing Demands of Built Detergents" D. Fumet (together with A. Dufour and P. Reeve), Rohm & Haas European Laboratories, Valbonne, France, was successful. With the above mentioned changes, the requirements of the polymeric co-builders used in combination with the primary builder have also evolved. What was considered to be the optimum co-builder in a more traditional formulation may no longer provide the desired performance in some of the more recently developed

Figure 5 Long-lasting effect with Sokalan® HP 70 – Contact angle measurement (Source: Heike Becker, BASF)

	after 1. rinse	after 2. rinse	after 3. rinse	after 5. rinse	after 8. rinse	after 10. rinse
Sokalan® HP 70	< 5	< 5	< 5	< 5	< 5	10 – 15
polycarboxylate	5 – 10	5 – 10	10 – 15	10 – 15	10 – 15	10 – 15
Bathroom cleaner	10 – 15	10 – 15	10 – 15	10 – 15	10 – 15	10 – 15
Bathroom cleaner + Sokalan® HP 70	< 5	< 5	< 5	< 5	< 5	10 – 15
Hydrophobically mod. Polycarboxylate	10 – 15	10 – 15	10 – 15	10 – 15	10 – 15	> 15
without	10 – 15	10 – 15	10 – 15	10 – 15	10 – 15	10 – 15

Table 1 Shortened drying times (min) (Source: Heike Becker, BASF)

Figure 6 Alkali-swellable emulsion – thickening effect (Source: S. Jaynes, CIBA Specialty Chemicals)

systems. As in non-phosphate bases for automatic dishwashing detergents the main cause for film formation is calcium carbonate due to high level of carbonate in the formulation combined with water hardness, low Mw acrylic homopolymers are efficient in controlling calcium carbonate precipitation. In this class of polymer, varying end-groups is a way to increase anti-scaling efficiency. It was demonstrated that phosphono end-groups are really the composition of choice and provide a significant reduction of glass filming.

Microcontainers, Textile Pilling, Liposomes for a Wellness Concept

Recently, the demand for textiles, which are finished for additional functions, was multiplied going beyond usual clothing-specific aspects. For such additional finishing of textiles as a function of the desired characteristics a broad pallet of active substances, like perfumes, bactericides, acaricides, insect repellents, pigments, enzymes, odor absorbers or phase change materials is available. Microencapsulation is a powerful tool to solve such problems. In this context, G. Engelmann (co-authors: M. Jobmann and G. Rafler), Fraunhofer Institute for Applied Polymer Research, Potsdam-Golm, Germany, described "Polymers for Microcontainer in Body Near Application" (see also [2]).

Generally, the preparation of a microcontainer is possible both by reactive and non-reactive procedures (s. Fig. 7). Based on monomer compounds core/shell structured microparticles can be prepared by reactive microencapsulation processes especially in combination with polycondensation

or polyaddition reactions. Polymers with special characteristics for selected requirements as microcontainer are convenient for non-reactive procedures to prepare matrix particles.

For matrix particles based on different types of polylactic acid (PLA) the hydrolytic resistance and the influence on the release properties were demonstrated. Changes in the polarity of modified polylactides, necessary for these effects, can be tailored by copolymerisation with polyethylene glycol (hydrophilic) or end-group modification with stearyl alcohol (hydrophobic). The release of the agent, initiated by hydrolytic degradation, was retarded by the hydrophobically end-group modified PLA. In comparison to the hydrophilically modified PLA that means only 50 % release with double length of time.

The increase of thermal stability of micro-capsules is possible by multiple encapsulations. Sometimes, from an economic point of view this procedure finds too little resonance. By polymeric surfactants (PE-MSA-copolymers) the in-situ wall forming process of reactive encapsulation procedures with MF-resins can be supported in favor of a more stable shell of the particles. This means renouncement of a secondary encapsulation.

In 'past times' the performance testing of laundering processes (detergents and washing machines) was often focused on soil and stain removal. Later, other performance parameters, such as incrustation, greying and tensile strength loss, were included in the performance tests. For the cleaning performance and a number of secondary performance properties international standardised evaluation methods

are developed. Since the application of cellulase in fabric detergents beneficial effects such as color restoration and pilling prevention, and adverse effects like cotton depolymerisation became an object of testing, both for the development of new detergents and for product testing.

On behalf of an international team, P.M.J. Terpstra, Department of Agrotechnology and Nutrition, Section Consumer Technology and Product Use, Wageningen University, The Netherlands, presented "A New Approach to the Evaluation of Textile Pilling". Although there exist a number of testing methods for textile pilling, at present no method is generally used for the evaluation of pilling prevention and/or pilling removal during laundering. This leads to the situation that the outcome of such tests depends on the method and institution that performs the research. Because of the consumer relevancy of this matter the Wageningen University has initiated a discussion on this subject with experts from different fields in a workshop structure. The aim of this project is three-fold:

- to create an overview on the testing methods presently used and their feasibility
- to compare and discuss their feasibility,
- and to discuss if one or more are suitable as a basis for general acceptance (standardisation).

The Participants of the Textile Pilling Workshop

P. M. J. Terpstra, Department of Agrotechnology and Nutrition, Section Consumer Technology and Product Use, Wageningen University, The Netherlands, F. Frey (EMPA, Switzerland), K. Gibson (Novozymes, Denmark), R. Hild (Research Institute Hohenstein, Germany), I. van Kessel (SOHIT, The Netherlands), E. Krijnen (Unilever, The Netherlands), R. Lodewick (P & G, Belgium), A. Ophüls (wfk, Germany), T. Rechenbach (Henkel, Germany), F. Schambil (Henkel, Germany), A. Schop (SOHIT, The Netherlands).

In the meetings the participating experts presented their available research data and experience on the topic. Thereafter several hypotheses on the appraisal of pilling were evaluated followed by a discussion on how a generally accepted testing method could be achieved. The project was run by an international group of experts in the field

of textile cleaning research, representing test houses, consumer organisations, detergent/enzyme manufacturers and universities.

The most relevant findings of the first session were that:

- textile pilling still is a major consumer concern,
- at the time being pilling can be assessed in comparative tests only,
- the development of pilling monitors is vital for a reliable evaluation of textile pilling and that
- by mechanical action artificially pilled test materials behave different compared to 'naturally' pilled materials and therefore are not suitable for the assessment of pilling due to laundering.

Furthermore, it was concluded that more specific research data was needed regarding the panel assess-

ment with forced ranking and about the suitability of a series of pilling monitors. This information was generated in a series of additional tests.

In a second session a complete outline of a pilling test could be defined. As there is not yet sufficient information about the reproducibility of the method it was decided that the participants would use the method for about one year to get experience with it. In that period a set of pilling monitors will be available. After that period, in a last session, the fine-tuning of the method will be achieved.

External laboratories that are familiar with the assessment of pilling are requested to join this evaluation.

"Perceivable Wellness Effects via a New Liposome Concept for Fabric Care" were demonstrated by W. Eisfeld¹ (co-authors: R. Wachter¹, R. Stürmer² and W. Boucsein²), ¹Cognis Deutsch-

land GmbH & Co. KG, Düsseldorf, and ²Institute for Physiological Psychology, University of Wuppertal, Germany. The 'Magic Wellbeing Triangle' is shown in Fig. 8. Based on the measurement of psycho-physiological parameters like skin conductivity, heartbeat and electrical muscle signals, 'Objective Emotional Assessment' (OEA) has been successfully introduced in recent studies ([3] to [5]) as a suitable methodology for evaluation of emotional consumer response. As this procedure provides information on the overall physical and mental level of contentment or disaffection, it allows substantiating product claims strongly linked to 'wellbeing'.

In the present study, OEA was applied for the first time to the evaluation of cotton textiles which were treated with fabric care formulations. In comparison to two benchmarks, water-only and esterquat fabric conditioner treatment, the performance of a new care formulation based on liposomes was evaluated. The treated fabrics were presented in two different modes: firstly, a piece of cloth was pulled over the arms of volunteers; secondly, the panelists were asked to move under light physical stress on a treadmill while wearing tailor-made cloaks.

From multivariate statistical analysis it was concluded that in comparison to the benchmarks the liposome formulation raises higher interest and attention, produces emotional excitement, is perceived as distinctly more pleasant, imparts higher ease of moving and thus provides an overall sensation of 'wellbeing' to the consumer.

Figure 7 Preparation of microcontainers (Source: G. Engelmann, Fraunhofer Institute for Applied Polymer Research – IAP)

Figure 8 The 'Magic Wellbeing Triangle' (Source: W. Eisfeld, cognis)

Foam Drainage, Rheology, Microemulsions, and Polymer Surfactants

In the focus of this year's *Basics* Section were foam drainage, rheology, and polymer surfactants. "The Physics of Foam Drainage" was presented by St. Hutzler¹ (co-authors: D. Weaire¹, A. Saugy¹, S. Cox² and N. Peron¹), ¹School of Physics, Trinity College, University of Dublin, Ireland, and ²Institute of Mathematical and Physical Sciences, University of Wales, Aberystwyth, UK (<http://www.tcd.ie/Physics/Foams/>).

Foam drainage describes the flow of liquid through a foam, driven by gravity and pressure differences. In a freely draining foam this leads to an ever decreasing liquid content, resulting in a considerably less stable *dry* foam (Fig. 9). In such a foam gas diffusion is enhanced and the thinner films

Figure 9 Free drainage results in the establishment of foams with a non-uniform liquid content – dry at the top, wet at the bottom (Photograph by J. Cilliers, Imperial College, London)

are also more likely to break. Foam drainage is thus an important factor for foam stability, and as such of great relevance to the detergent industry.

Over the last decade substantial progress has been made in understanding the relevant physics behind foam drainage and the related issue of drainage or creaming in emulsions [6]. This was instigated largely by so-called forced drainage experiments, in which the foam is fed at the top with a supply of liquid at a constant rate (Fig. 10). This results in a rather sharp interface between wet and dry foam moving downward with a constant speed. The propagation of this so-called solitary wave may be monitored either with a digital camera or measurements of electrical conductivity.

The experiment was crucial for the development of a foam drainage equation which is able to predict the observed solitary wave, but also the spatial and temporal variation of liquid fraction in free drainage experiments. The equation is based on the assumption that liquid flows mainly through the network of plateau borders (intersections of three films). The cross section of the borders and the size of the

nodes in which they meet are not fixed but adapted to the local flow rate of the liquid (Fig. 11).

The boundary conditions for the flow of liquid through the plateau borders are set mainly by the surface shear viscosity. Two extreme cases are readily accessible to theory: rigid interfaces, as in protein foams, result in an essentially parabolic flow profile, fully mobile interfaces, as for certain surfactants, lead to a uniform flow velocity across a plateau border.

Current work includes detailed computer simulations of the local flow through nodes in order to deal with the more realistic case of a finite surface mobility. Complementary to this are attempts to determine this mobility experimentally, using forced foam drainage experiments.

A somewhat harder problem appears to be the observed convective bubble motion in foams with high liquid content since this requires a detailed understanding also of foam rheology, i.e. the behaviour of foam under an applied stress.

In summary, forced drainage has turned out to be an invaluable techni-

que for the investigation of liquid foams and offers great potential for the design of novel foam characterisation procedures.

**Basic Research Award
(Förderpreis Grundlagenforschung)
to Judith Schulze-Schlarmann**

On the occasion of the First European Detergents Conference 2005 in Würzburg Dr. Judith Schulze-Schlarmann was awarded the Promotional Prize “Basic Research Detergent Chemistry” of the Expert Group Detergent Chemistry of the Society of German Chemists (GDCh) for her thesis “About the interfacial behaviour of nonionic surfactants: adsorption, surface forces, film stability” in appreciation of her innovative and sound work about the properties of thin liquid films. As a result *Judith Schulze-Schlarmann* deepened the understanding of interactions in liquid films. The main impact of her work is to find in the extended potential to control the properties of surfaces, liquid films and foams by variation of the surfactant structure.

Judith Schulze-Schlarmann studied chemistry at the University of Cologne from 1996 to 2001 and obtained a diploma degree in the research group of Prof. R. Strey for her work on “Recovery and characterisation of interfacially pure surfactants”. In 2004 she concluded her doctorate thesis also under R. Strey. At the beginning of 2005 she joined Engelhard Process Chemicals GmbH, Hanover, as a Sales Representative for Europe.

Many solutions of ionic or non-charged surfactants exhibit striking viscoelastic features. *H. Rehage* (co-authors: *Manuela Pflaumbaum*, *P. Fischer* and *R. Fuchs*), University of Dortmund, Germany, delivered a “Quantitative Description of the Rheological Properties of Viscoelastic Surfactant Solutions”. These phenomena can, for instance, be observed in dilute solutions of entangled, rod-shaped surfactant micelles. In the regime of small deformations, shear stresses or shear rates, the dynamic features of the viscoelastic solutions are characterised by the equations of a *Maxwell* material. Such simple relationships can be traced back to the limited average lifetimes of the micellar aggregates. At elevated values of the shear stress or

deformation, however, more complicated properties as normal stresses, stress overshoots or shear-thinning behaviour occur. All these phenomena are quantitatively described by a constitutive equation, which was first proposed by *Giesekus*. The phenomena, discussed in this lecture, are of general importance and can be equally observed in different materials, such as polymer or protein solutions. The viscoelastic surfactant solutions can, therefore, be used as simple model systems for advanced studies of fundamental rheological principles.

Stable dispersions of either gas bubbles or solid particles like abrasives become increasingly attractive for the home care market. The property to yield a stable dispersion is not necessarily linked to a high viscosity in general but requires highly viscous, solid-like behaviour under rest as well as liquid-like flow behaviour under shear.

In this context, *R. Scheuermann* (co-authors: *J. Meyer J. Peggau* and *Karin Fürch*), Degussa AG, Care Specialties, Essen, Germany, discussed "Rheology with Vesicle Gels".

A gel comprising such a yield zone can be obtained by creating multi-lamellar vesicles with a rather stiff shell. Due to the attractive forces of the opposite electrostatic charges the combination of suitable anionic and cationic surfactants yields vesicles that are inflexible enough to comprise a yield zone.

Surfactants which are appropriate to yield suitable vesicle gels can be chosen according to their spatial dimensions since the geometry of the molecules determines their aggregation behaviour. In order to achieve an even distribution of vesicles resulting in a system with a pronounced yield zone the use of a long-chain spacer molecule such as PEG-80 Glyceryl Cocoate

which separates the individual vesicles is advisable.

The existence of a yield zone can be shown using oscillatory rheology. With this method a segregation of the elastic and the viscous part of the complex shear modulus is possible thus describing the solid-like and the liquid-like character of a sample. An approximate quantification of the yield zone which allows the comparison and characterisation of different formulations is possible as well.

The "Simulation of Microemulsions with Dissipative Particle Dynamics" was performed by *Sarah G. Schulz*¹ (co-authors: *U. Frieske*¹, *H. Kuhn*¹, *R. Strey*², *F. Müller*³, *C. Mund*³ and *J. Venzmer*³), ¹CAM-D Technologies GmbH, Essen, ²Institute for Physical Chemistry, University of Cologne, and ³Degussa, Goldschmidt GmbH, Essen (see also [7] to [11]). Complex-structured self-assemblies such as colloidal suspensions, micelles, immiscible mixtures, microemulsions, etc., represent a challenge for conventional methods of simulation due to the presence of different time scales in their dynamics. Recently, a novel computer simulation technique, Dissipative Particle Dynamics (DPD), was successfully applied to model the behaviour of diblock copolymers at the water/oil interface. With the use of a simple model simulations of polymer/water/oil systems were performed at different concentrations.

In this lecture the results of nano-scale 'coarse-grained' simulations with DPD were presented. DPD is a meso-scale simulation technique that has been introduced in order to simulate three-dimensional structures of organic polymer aggregates.

In DPD the polymer is modeled using particles which are interacting by conservative, dissipative and random forces. Particles are not regarded as molecules but rather as droplets or clusters of molecules.

This technique has been successfully applied to simulate the three-dimensional structures of microemulsions, e.g. the bicontinuous phase of $C_{10}E_4$ in water and *n*-decane, in domains of less than 100 nm. The different structures of the polymer/water/oil system were effectively characterised with DPD and are in remarkable agreement with the experiment. Even the so-called 'boosting-effect', a concentration-shift caused by the partial substitution of the polymer, was successfully simulated.

The DPD method proved to be a reliable tool to get a better understanding of the nanostructure of self-assemblies

Figure 10 In forced drainage experiments surfactant solution is added onto a dry foam at a fixed flow rate (a). This results in the propagation of a drainage wave through the foam (b). The vertical profile of liquid fraction can be monitored in time by measurements of optical transmission or using segmented electrodes and monitoring electrical capacitance, as in the experiment shown here. (Source: *St. Hutzler*, Trinity College, University of Dublin)

Figure 11 Simulations of the flow through nodes are challenging due to the complicated shape of the node. Shown are flow velocity profiles for the two extreme cases of Poiseuille flow (left) and plug flow (right). Of particular interest is the case of a finite surface mobility, as in many surfactants (middle). (Source: *St. Hutzler*, Trinity College, University of Dublin)

and is therefore applicable to support the often complicated experiments or even to obtain experimentally unavailable data.

Fig. 12 shows at a polymer concentration of 0.12 mol % an o/w emulsion at a water/oil ratio of 8:1 and a L₃ bicontinuous phase emulsion at a water/oil ratio of 1:1 (water phase removed).

“Polymer Surfactants – Novel Agents with Exceptional Properties” were presented by J. Storsberg (co-authors: S. Garnier and A. Laschewsky), Fraunhofer Institute for Applied Polymer Research. Features of polymeric amphiphiles are extremely low cmc’s, stable micelles even at high dilutions, adjustable aggregate size by macromolecular design, decoupling of surfactant properties, e.g. surface activity and solubilization $\Rightarrow$ independent optimisation, broad variation of properties, such as foaming or viscosity, adjustable compatibility of the hydrophobic polymer block for a given solute, efficiency boosting, control of behaviour by external stimuli (‘surfactant on demand’), e.g. by pH, temperature etc. (special feature of polymers). That means, macrosurfactants offer more performance for less material.

Applying new strategies to block copolymers, for instance, the so-called reversible addition fragmentation chain transfer (RAFT) a plethora of new amphiphiles is available (Fig. 13) which show, for instance, weak or no foaming. Switchable ('smart') surfactants enable a temperature-induced change of the hydrophilic/hydrophobic balance (Fig. 14). Multi-sensitive triblock copolymers such as poly(styrenesulfonate)-block-poly(betaine)-block-poly(vinylbenzoic acid) allow a combination of pH switch and salt switch in aqueous solution. The switching of polymer blocks can be even done step by step.

As polymers are generally harmless polymer surfactants have a high potential for virtually any application in detergents, cosmetics, body care or even medicine.

Product Safety, Low-Temperature Laundering, Dishwashing, and Legislation

The *Legislation* Section comprised product safety with special focus on perfumes, administrative control, hygienic aspects in low-temperature laundering and consumer habits and practices in dishwashing. "The Ever-changing Legislative World of Detergents and

Cleansers in Europe" was highlighted by R. Schröder, Henkel KGaA, Düsseldorf, Germany.

Most detergents and cleansers entering the market are covered by

the chemical legislation that is currently revised by the European Union (REACH = Registration, Evaluation, and Authorisation of Chemicals), and the Detergent Regulation that came into

Figure 12 DPD simulation: a) o/w emulsion at a polymer concentration of 0.12 mol % and a water/oil ratio of 8:1 and b) L_3 bicontinuous phase emulsion at a polymer concentration of 0.12 mol % and a water/oil ratio of 1:1 (water phase removed) (Source: Sarah G. Schulz, CAM-D Technologies)

Amphiphilic Block-Copolymers by RAFT

- **hydrophobic block fixed, much above glass transition**
- **large variety of hydrophilic blocks**

Figure 13 New polymeric amphiphiles by RAFT technology (Source: J. Storsberg, IAP)

Switchable ("Smart") Surfactants

temperature induced change of the hydrophilic/hydrophobic balance

Figure 14 Switchable ("smart") surfactants (*Source: J. Storsberg, IAP*)

force on October 8th, 2005. In addition, there is supplementary legislation on certain products (e. g. biocides and products with extreme pH value). It is not only the complexity of the legislation that is putting a heavy burden on industry, but the speed of the change as well. How should industry cope with this situation? The detergent and cleanser industry has traditionally played an active role and made a lot of effort to maintain a high level of environmental and consumer protection. The A.I.S.E. Code of Good Environmental Practice, the HERA project (www.heraproject.com), and the A.I.S.E. Charter for Sustainable Cleaning (www.sustainable-cleaning.com) may serve as examples. It is of paramount importance to intensify the communication with stakeholders and legislators about the industry's efforts and achievements. The communication should not only focus on success stories but should also incorporate critical issues like errors and failures. The A.I.S.E. Code of Good Environmental Practice may serve as an example. The target of reducing the energy per wash was only partly achieved since the consumer didn't follow industry's advice to lower the washing temperature. On the other hand, the reduction of poorly biodegradable organics (PBOs) was a clear success since the detergent and cleanser industry is in control of the formulas and could choose appropriate raw materials.

Perfumes are important detergent constituents because they subdue the odor of other detergent ingredients and they convey a characteristic odor to the detergent. Synthetic fragrances are important components of such perfumes. These materials are also subject to the new EU chemicals legislation (REACH). J. Tolls, Henkel KGaA, presented "Fragrances and REACH – An Approach for the Ecological Evaluation of Fragrance". Under REACH, chemicals may only be marketed if they can be demonstrated to be safe. In order to find out whether or not individual fragrance materials may be used in the future, Henkel performed a simple and conservative screening environmental safety evaluation of the low tonnage fragrance materials. As part of this exercise the environmental product safety data were inventorised and a chemical risk assessment was performed.

The results indicate that more than some 75 % of the fragrance materials in the low to medium tonnage range (1 to 60 tons used per annum) can be

considered safe to use on the basis of presently available data. A synopsis of the risk assessment results and the input data was performed to learn which additional data is required. In the case of substances without effect data, reduction of the assessment factor from 10,000 to 1,000 by replacing QSAR-based estimates of acute toxicity with experimentally determined data on acute toxicity in *Daphnia* is sufficient to result in demonstration of safe use. At a cost of less than Euro 5,000, this is a promising approach for an additional 30 substances. Alternative cost-efficient options for improving the risk assessment results are testing for ready biodegradability, refining the use estimate, or targeted testing for effects.

"Detergents and Cleansing Agents in the Focus of Administrative Control" were highlighted by Evamaria Kratz, Ministry for Food and Rural Regions, Stuttgart, Germany. The official survey of detergents and cleansing agents ensures protection of environment by surveillance of the EC Regulation on Detergents and the Washing and Cleansing Agents Act. It also ensures the protection of the consumer, which is stipulated in the German Food and Feed Act and the Chemical Law. Additionally, some new criteria in respect of human health are now given by the EC Regulation on Detergents. The implementation of these provisions is task of the Federal States ('Bundesländer') and is carried out in different ways.

Inspections of manufacturing premises, analysis of product samples and evaluation in regard of the legal regulations are current themes of the daily work of the competent authorities and the enforcement laboratories.

The procedures of inspections, analysis and evaluation were described, whereby the connection of the different fields of law was demonstrated.

For clarification topical cases are demonstrated, for example the analysis of fragrance allergens as citral, geraniol and limonene. They must be labelled over 100 mg/kg. Therefore the consumer with allergies has the possibility to check the ingredients and avoid products which can be harmful for him. Also the declaration of preservation agents, which shall be listed irrespective of their concentration, is a new regulation especially for consumers with allergy problems. Recurrent critical points were discussed, such as:

- Products similar to food are considered critically by the authorities in regard of the fact that children often eat or drink of it.
- Instructions for use are sometimes difficult to understand and provoke therefore improper use.
- Labelling of hazardous substances is often without enough attractive attention and will therefore not be realized by the consumer.

"Hygienic Aspects at Low-temperature Laundering" were discussed by W. Lichtenberg, HAW Hamburg, F. Girmond, Research Institute Hohenstein, R. Niedner, EvB-Klinikum Potsdam, and I. Schulze, B/S/H Spandau, all from Germany. Laundering at temperatures below 60 °C is increasingly practised because of environmental relief and according to textile labelling. Cleaning efficiency at 30° and 40 °C is studied extensively by detergent producers and washing machine manufacturers. In this context, hygienic aspects have to be discussed as well. The lecture was concerned with three points of view:

- Is the germ charge of the textiles sufficiently reduced?
- May germs (possibly proliferated in a poorly vented washing machine) be transferred on textiles?
- Is it indicated to worry about general health hazards?

The microbiological situation was discussed in detail on the basis of experimental investigations. It follows that the risks are negligible under normal circumstances, so that low-temperature laundering is highly recommendable for ecological reasons. From aesthetic considerations only some provisions like sufficient ventilation and dry storage of the textiles are advisable.

"Consumer Habits and Practices in Manual Dishwashing in Europe" were summarised by R. Stamminger, University of Bonn, Section Household and Appliance Technology (co-author: Gisela Goerdeler, Deutscher Hausfrauen-Bund e.V., Bonn), Germany. In seeking to understand and prevent global warming and other man-made environmental defects, the resource consumption of household appliances has come under close scrutiny. One household task – dishwashing – can be accomplished by an appliance, by hand, or by some combination of the two. To investigate the environmental effects of these competing methods tests comparing the energy, water and cleanser consumption and performance of

manual dishwashing with dishwashing machines were conducted. Additionally, information about daily practice of manual and automatic dishwashing was collected.

The first learning is that manual dishwashing is done in many different ways with very different amounts of resources used (for water consumption see Fig. 15). The second learning is that almost everyone does the manual washing up always in the same way. As third it was learned that washing up smaller loads is tentatively causing higher specific consumptions (see Table 2). And finally, the fourth leaning is that dishwashers do a better job with less consumption of resources than any of our test persons could do.

But, as manual dishwashing will never get obsolete, the target to reduce environmental effects can only be

achieved, if also the manual dishwashing gets improved in daily practice. Under the umbrella of "Forum Waschen" in Germany a nation-wide action day ("Aktionstag Nachhaltiges Waschen") will try to address the issue of dishwashing to German households at the next event on May 10th, 2006.

Market: "Stinginess becomes stale"

The Society for Consumer Research (Gesellschaft für Konsumforschung – GfK) continuously scans the development of all markets and brands by means of representative consumer panels. The main instrument is the 17,000 household panel Consumer-Scan which accurately ascertains the purchase of goods for daily usage (Fast moving consumer goods – FMCG)

with In Home Scanning. This data in conjunction with other ascertained influential variables constitutes the base for the so far most extensive empirical documentation concerning the central question, how it is possible in a discounting environment to achieve value creation instead of value depreciation.

"Premium or Cheap – What is the Future of Home and Personal Care Products?" asked W. Twardawa, GfK Panel Services Deutschland GmbH, Nuremberg [12]. Based on the effective purchase behaviour in 150 categories the target group *Premium-Shopper* (20% of all households) was identified which aligns its purchase decisions with the added value of the respective brand and is as well willing to pay a higher price for that value added. The potential of this target group, which is not only freshness- and adventure-oriented but as well interested in innovations, is clearly higher. Declining real household net incomes drive the consumers to discounters and private labels causing in turn the brand manufacturers and full-range suppliers to react with heavier price promotions. Wrong way: This leads to value decrease or even destruction. In addition, this way brand-shoppers are educated to be promotion-shoppers, who then pick private label products more easily.

For home and personal care products the pricing pressure continues to be high. Since 2000 the share of turnover of the discounters and drug-stores increased for home care from 48 to 58% and for personal care products from 53 to 59%. Despite the further increase of private labels Lidl focuses on manufacturer brands again. ALDI wants to follow. For high-income consumers the stinginess becomes stale. They are willing to pay more for an added value. Thus, for the first time in years a decline in price orientation in favor of quality orientation can be observed. By offering a clear recognizable added value more than every third private label buyer can be won back for manufacturer brands.

The strategy development should be based on the differentiated examination of the particular category specifics. Successful premium strategies can also be found in the 'swamp' of commodities. Premium brands are next to the private labels the only growth segment and especially provide opportunities to medium-sized companies. The key points of success for sustainable corporate policy are clear positioning (no more average), continuity in the core, but adaptation to the chang-

Figure 15 Histogram of water consumption of 113 test persons from all over Europe washing up 12 place settings of dishes under standardised conditions (Source: R. Stamminger, University of Bonn)

Results per 'place setting'					
From tests cleaning 12 'place settings' + additional tests cleaning '2 place settings'					
Average values per place setting Test series in Europe	Number of test persons	Water in Litre	Energy in kWh	Time in min	Cleanser in gram
Cleaning of 12 'place settings'	113	8.6	0.21	6.6	2.9
Cleaning of 2 'place settings'	46	10.1	0.21	8.6	3.8
Weighted average per 'place setting'		9.0	0.21	7.2	3.2
For comparison: Dishwasher		1.0–2.0	~0.1	<2 ~10	(~2.5)

Table 2 Comparison of resources used per place setting for manual washing up different amounts of dishes under standardised conditions coming from two different test series. Additionally, a weighted average per place setting is given for manual washing up and for comparison reasons also for automatic dishwashing (Source: R. Stamminger, University of Bonn)

ing environment and of course innovations. But not only big steps help – detailed work is needed.

European Detergents Conferences 2006 and 2007

Please mark your calendars for the

- 53rd SEPAWA Congress incl. the 2nd European Detergents Conference (EDC): Oct. 11–13, 2006
- 54th SEPAWA Congress incl. the 3rd EDC: Oct. 10–12, 2007.

These Congresses will again take place in the Congress Centrum Würzburg.

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