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Hairs, Cars, Textiles: In Quats We Care

Abstract

We care about many surfaces we encounter in our daily lives: Our hair, the paint surface of our cars, the fibres of our clothes, just to name a few. A common feature of almost all of such surfaces is that they carry anionic charges. Therefore it is not surprising that the deposition of caring ingredients is typically done by using cationic amphiphiles, so-called quats. Depending on the type of application and the effect desired, the quats can be based either on organic surfactant chemistry or on organomodified silicones. The general chemistry, formulations, mode of action and recent trends will be discussed for several applications. One topic will be the use of cationic microemulsions as rinse aids in the car wash. Hair conditioning today means more than just improving combability or feel; more recent requirements also include benefits concerning e.g. heat and UV protection. Finally, the performance of fabric softeners can be correlated with properties of the vesicle dispersions; additional benefits concerning fibre care can be obtained using silicone quats.

Introduction

Many surfaces we deal with have to be protected against influences of the environment. In some cases the method of choice is the forced deposition of caring substances, e.g. the application of creams and lotions onto our skin. In many other applications, however, the deposition of the caring ingredients is desired from a more diluted aqueous formulation. Ideally, there should be some attractive force between the benefit agents and the substrates to be treated. In nature, such interactions are typically based on a key-lock-mechanism, utilizing specific shapes and multiple H-bonds, e.g. in the specific recognition between antigen and antibody. Most practical surfaces we care about, such as hair, paint, textiles, are too diverse to utilize this principle, but luckily there is one common feature of many of those surfaces: Most of them carry an anionic surface charge. Therefore, the deposition mechanism in these cases can be based on Coulomb interaction with cationic substances, mostly cationic surfactants. These so-called quats can be based either on oleochemistry or on silicone chemistry; the hydrophobic portions of the quats are either alkyl chains as derived from natural triglycerides, or polydimethylsiloxane, respectively. The choice of the molecular architecture will depend on the desired effect in the specific application.

Car Wash

Mode of Action of Rinse Aids

Many consumers make use of automatic car wash facilities to get the exterior of their cars cleaned. The majority, however, is probably not aware of what is happening there from the perspective of interfacial chemistry to render the cars spotlessly clean. The removal of soil from the surface of a car is rather straight forward: surfactants/dispersants are solubilizing and dispersing oily and hydrophobic soil, which is then washed away by rinsing with water **(Fig. 1a)**. Whether the car exits the automatic car wash facility shiny and spotless and hence the customer is satisfied, however, is determined by the action of the so-called rinse aid. This is the most crucial step of the entire car wash process. The surface chemistry involved is shown schematically in **Fig. 1b**. After the soil has been removed, the rinse aid is applied, which basically consists of a very diluted cationic microemulsion, *i.e.* very small (<100 nm) oil droplets stabilized by cationic surfactants. Because of the Coulomb attraction between the anionic surface of the car and the cationic surfactants, the surfactants attach to the paint surface and expose their hydrophobic tails (and the oil phase) towards the water phase. Therefore, a few seconds after the rinse aid has been sprayed onto the car, its surface gets hydrophobized, the water film breaks and recedes; this is called sheeting and beading. In the final blow drying step, only the last few water drops have to be removed, which is a major benefit considering the greatly reduced energy consumption. And there is a good chance that the car leaves the car wash spotless and glossy.

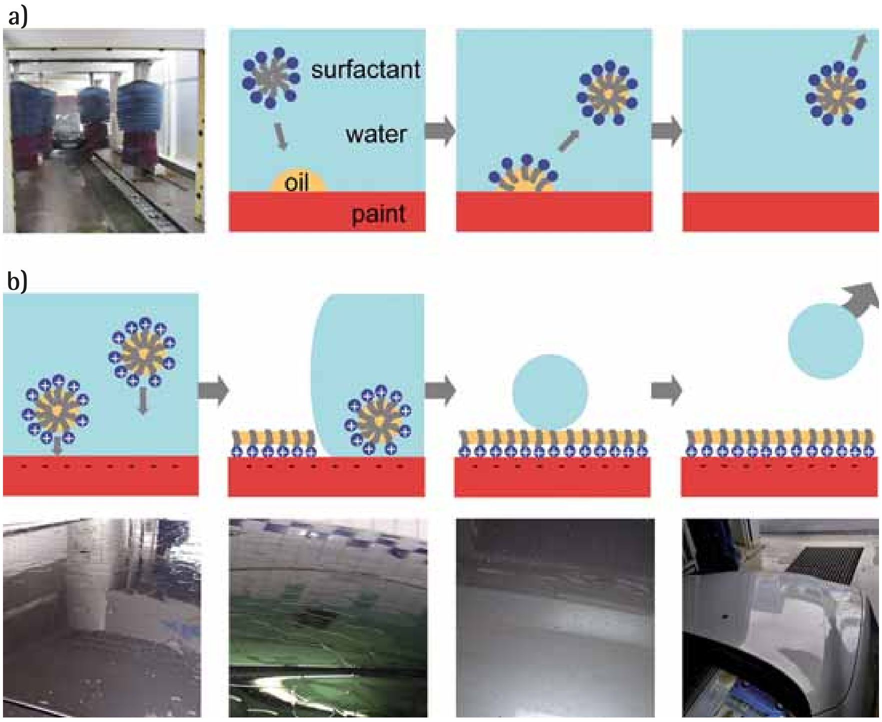

Fig. 1 Surface chemistry in the car wash: **a)** Soil removal by surfactants; **b)** Action of the rinse aid: Sheeting and beading

Formulation of Rinse Aids

Concerning the formulation of rinse aids, there are a number of requirements to fulfill. Since the emulsions sprayed onto the cars are typically very dilute, most of those requirements concern stability and dilutability: The rinse aid concentrate should be clear and stable at temperatures between 1 and 40°C, and dilutable in all ratios with water down to 1:1000, not affected by the local water qualities used. These are features which could be achieved using microemulsions, which are by definition thermodynamically stable mixtures of oil, water and surfactant, with droplet sizes in the nm range. Because of the low content of oil phase, one is quite far away from the classical model system water/oil 1:1 with the typical fish diagram (1, 2). However, the spontaneous formation of the droplets in the nm range without shear force, the stability and dilutability indicate that these formulations are »real« microemulsions in scientific terms. This has the advantage that one can utilize the key learnings from microemulsions in general to successfully formulate rinse aids. Traditional formulas contain at least the following raw materials: Highly effective dialkyl dimethyl quats, inexpensive glycol, mineral oil, highly effective coemulsifiers based on amine chemistry, gloss additives and water. In recent years, increased focus has been put on the environmental impact, i.e. biodegradability, and hence the formulations have changed. Limited biodegradability of the dialkyl dimethyl quats was the reason why they are not used any more as fabric softeners in many countries; they have been replaced by so-called esterquats, carrying a hydrolyzable ester group between the alkyl chain and the quaternary nitrogen. Such diesters of di- or trialkanolamine are readily biodegradable, have an acceptable aquatic toxicity and can be used to formulate rinse aids with good performance. Concerning the oil component, the desired properties are low viscosity and low pour point. It turned out that some cosmetic oils like ester oils or diethylhexyl carbonate can be used advantageously instead of mineral oil. Often combinations of oils are used to obtain the application performance desired, i.e. the combination of sheeting efficiency, speed, and gloss. While in the past mostly ethylene glycol *n*-butyl ether has been used, today this has been replaced for environmental reasons by e.g. propylene glycol *n*-butyl ether. Many traditional formulations contain co-emulsifiers based on amine chemistry. Because of their aquatic toxicity, they should be replaced by alkoxylated fatty alcohols. By adjusting the amount of these basic components of the rinse aid formulations, the desired performance profile can be obtained, e.g. faster sheeting by increasing the amount of the substantive additives. In order to boost the application performance and to obtain premium products, performance additives have to be incorporated. By adding e.g. silicone quats, it is possible to provide the benefits the customers are looking for, like higher gloss for a longer period of time. But it always has to be taken into account that all additives need to be compatible with the cationic microemulsion formulations.

■ Hair Care

Hair Conditioning

Human hair has a complex fibre structure; most obvious from microscopy images is the outer layer, the cuticula, which protects the inner part, the cortex. Day in and day out, our hair is exposed to a variety of natural and/or artificial influences, such as UV light, mechanical stress, perming or bleaching. This causes mechanical and/or chemical damage of the cuticula and eventually of the entire hair structure, which typically leads to increased roughness. As a consequence, the hair gets hard to comb, feels dull and its gloss is reduced. Conditioning means to prevent, retard or to mask such changes. Since in damaged hair anionic groups get exposed, it is not surprising that the deposition of conditioning agents is again done by utilizing the Coulomb attraction to cationic compounds. This deposition of cationic conditioning ingredients is done most efficiently in an additional conditioning step after the washing process. Since the surfactant systems of shampoos are typically anionic, the deposition of cationic ingredients through the wash can only occur via the precipitation of insoluble 1:1-complexes between the cationic compounds, anionic surfactants and eventually other more hydrophobic ingredients. During the washing procedure, these complexes are solubilized by the excess of anionic surfactant. During the rinsing step, precipitation occurs, hopefully on the hair surface. This is the basic concept of conditioning shampoos, the so-called 2-in-1-shampoos.

Perfomance Evaluation of Conditioning Formulations

During the development of new conditioning agents, their application performance needs to be examined. First, this is done in laboratory tests using hair swatches, assessing parameters such as wet and dry combing force, wet and dry feel, gloss, curl retention, volume and static fly-away. The intermediate stage before the consumer test is a so-called half head test in which two formulations can directly be compared. Even more importantly, this method allows to assess the in-use properties, i.e. whether the conditioner feels nice to the touch during application and rinsing. This aspect should not be neglected, since consumer preception is one of the most critical success factors for any cosmetic product on the market, often more important than subtle differences in the intended effect, in this case the conditioning performance. It also has to be taken into account that different hair types or qualities have different individual needs concerning the various conditioning properties; therefore the formulator typically uses – if possible synergistic – combinations of several conditioning ingredients in order to address the specific customer needs. Here, only the basics and some new trends concerning conditioning ingredients can be discussed.

Formulation of Conditioning Rinses

Very basic conditioner formulations mainly consist of a dispersion of C16/18-fatty alcohol and one or more cationic surfactants in water. Popular cationic surfactants for this purpose are cetyltrimethylammonium or behenyltrimethylammonium chloride (INCI Cetrimonium or Behentrimonium Chloride). The most important properties these are able to provide are excellent basic conditioning, i.e. the hair gets easy to comb (wet and dry) and feels soft and smooth. Additionally, these quats lead to a rich appearance of the formula and pleasant in-use properties. As readily biodegradable alternative without sacrificing performance, again ester quats (e.g. INCI Distearoylethyl Dimonium Chloride + Cetearyl Alcohol) have been introduced recently.

Deposition of Conditioning Ingredients

In order to be most efficient, the conditioning ingredients should deposit preferentially at the regions with exposed anionic charges, as hypothesized above. This can be proven experimentally by fluorescence labelling of the conditioning ingredient and then localizing it on the hair surface by fluorescence microscopy. This fluorescence labelling is not possible with low molecular weight organic quats without greatly altering the deposition properties, but for polymeric silicone-based conditioning agents this method has been applied successfully several times. The first silicone conditioning agent we have used for this procedure consisted of a silicone backbone with both polyether and amino groups attached (INCI: Methoxy PEG/PPG-7/3 Aminopropyl Dimethicone). By comparing a reflection image (showing the topography only) with the corresponding fluorescence image (showing the location of the conditioning agent) of a treated and rinsed hair, it is obvious that this cationic silicone does not deposit evenly, but preferentially at the steps of the cuticula and damaged areas **(Fig. 2)**. This conditioning ingredient does not only deposit as expected, it also provides applicaton benefits which go well beyond basic conditioning: It increases the body and volume and helps curl retention, and because of the presence of hydrophilic polyether groups, it can be incorporated easily into formulations.

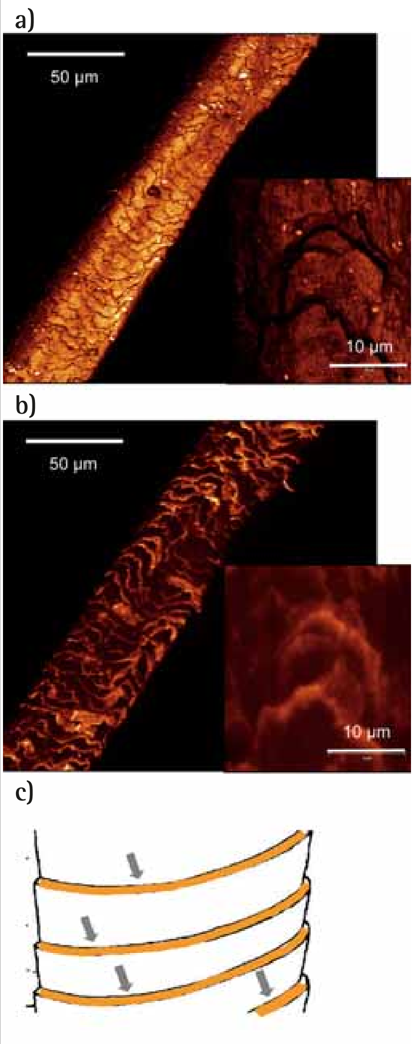

Fig. 2 Deposition of hair conditioning ingredients as shown by fluorescence microscopy: **a)** Reflection image of hair treated with conditioner rinse containing fluorescently labelled silicone conditioning agent; **b)** Corresponding fluorescence image of the same area; **c)** Schematic drawing of the selective adsorption of the silicone conditioning agent to the steps of the cuticula

New Silicone Quaternium-22: Structure and Conditioning Performance

Any new conditioning ingredients should address the following aspects in order to have a chance to be successful: Additional application benefits beyond wet and dry combability, superior sensory impression during and after use, and – last but not least – ease of use and flexibility for the formulator. Whether the classic silicone quats like Quaternium-80 consist of a silicone backbone with one quaternary group on each end, the Silicone Quaternium-22 recently introduced has a T-shape and accordingly carries three quaternary groups **(Fig. 3 a)**. This unique molecular architecture provides a novel combination of features (3): The significant improvement in conditioning performance when added either to a standard conditioner formulation containing Cetrimonium Chloride or to a basic shampoo formulation containing cationic Guar is shown in **Fig. 3 b** and **Fig. 3 c**.

Application Performance of Silicone Quaternium-22 beyond Conditioning

A relatively new claim concerns the heat stability of hair. Hair is subjected to thermal stress already by blowdrying, but even more by using high temperature styling devices as commonly used for curling or straightening. This thermal stress causes damage of the keratinous structure. The level of damage can be quantified by measuring the denaturation temperature by Differential Scanning Calorimetry (DSC). It could be shown by a test using a hair straightener at 180 °C that the new Silicone Quaternium-22 is able make the hair less susceptible to thermal damage **(Fig. 4 a)**. As hair coloring is becoming increasingly popular, another important claim concerns color protection, i.e. the reduction of color fading by application of shampoo. Already after a single wash, the difference (ΔE) in coloristic values (CIE-L*a*b color meter) before and after shampoo treatment is reduced by the addition of Silicone Quaternium-22 to the shampoo; after repeated washing cycles the effect becomes even more pronounced **(Fig. 4 b)**. While this claim is decidedly attractive as it is a property perceivable by the customer, even more immediate sensorial benefits could be found by a trained panel in a hand wash test with a simple shampoo formulation based on ethersulfate and betaine: Most of the eight parameters evaluated (e.g. foam creaminess, skin smoothness, skin softness) were significantly improved by adding 0.5% of Silicone Quaternium-22 **(Fig. 4 c)**. For the formulator, an attractive feature is the easy processing and the versatility of this new conditioning ingredient.

New Polysilicone-19

Fading of color will also happen upon exposure to sunlight. Especially the UV-portion of the sunlight also causes a reduction of tensile strength of the hair fibres. Therefore, there are ingredients on the market to provide some protection against UV-light, a kind of suncreen to be added to a shampoo or conditioner. Some of these products carry a cationic charge (e.g. INCI Polyquaternium-59, Polyamide-2), or are nonionic (e.g. INCI Polysilicone-15). A recent progress in this field was the introduction of Polysilicone-19 (INCI) (4): It consists of a siloxane backbone, with both methoxycinnamic acide esters and cationic groups attached **(Fig. 5 a)**. Therefore it combines the silicone character for superior conditioning, the cationic charge for deposition and absorbing groups for protection against UV. The color protection has been quantified by measuring the coloristic changes (ΔE) after UV irradiation with a sunlight simulator (equivalent to twice the natural daily dose at 50 ° latitude). For these measurements, a series of conditioners has been used, containing the various UV-absorbers mentioned

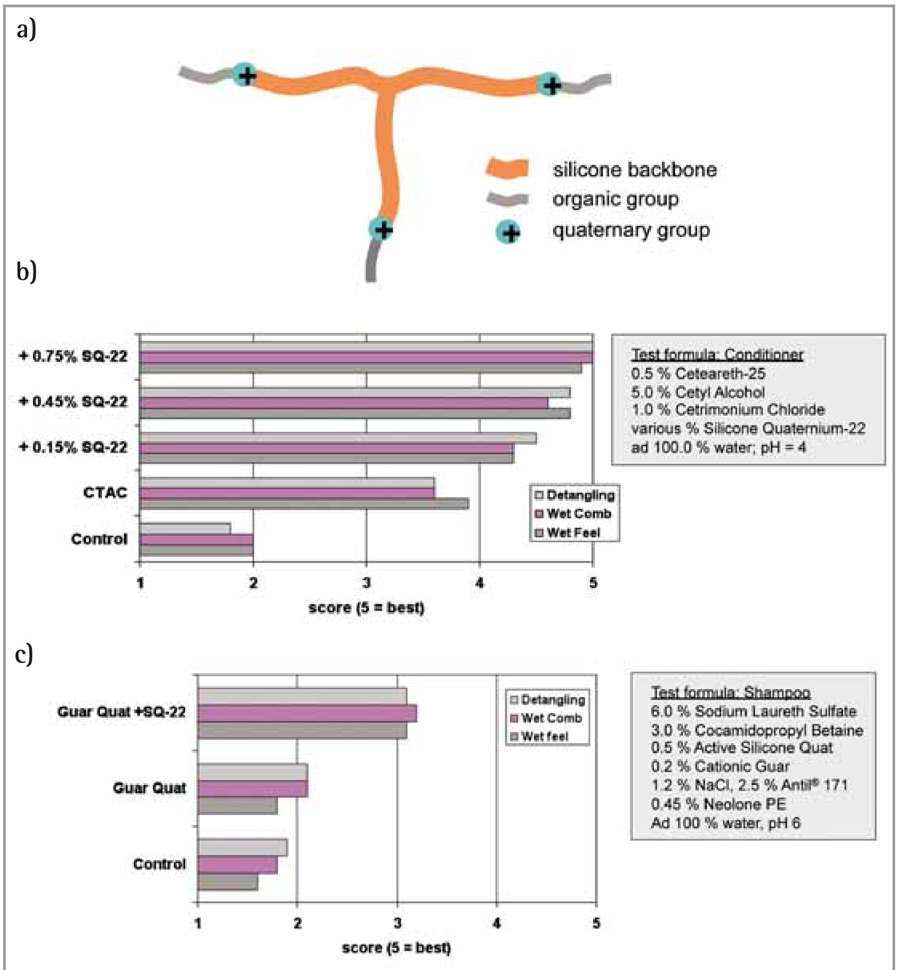

Fig. 3 Silicone Quaternium-22: **a)** Schematic chemical structure; **b)** Conditioning effect via conditioning rinse; **c)** Conditioning effect via shampoo

above. The data in **Fig. 5 b** show that Polysilicone-19 provides about 40% less color fading. At the same time, this effect is not at the expense of the excellent conditioning performance (Fig. 5C). It will be interesting to observe which other new claims for hair conditioners will come up in the future. For sure, they will somehow have to address the megatrends driving the cosmetic industry, e.g. health, anti-ageing, sustainability or convenience.

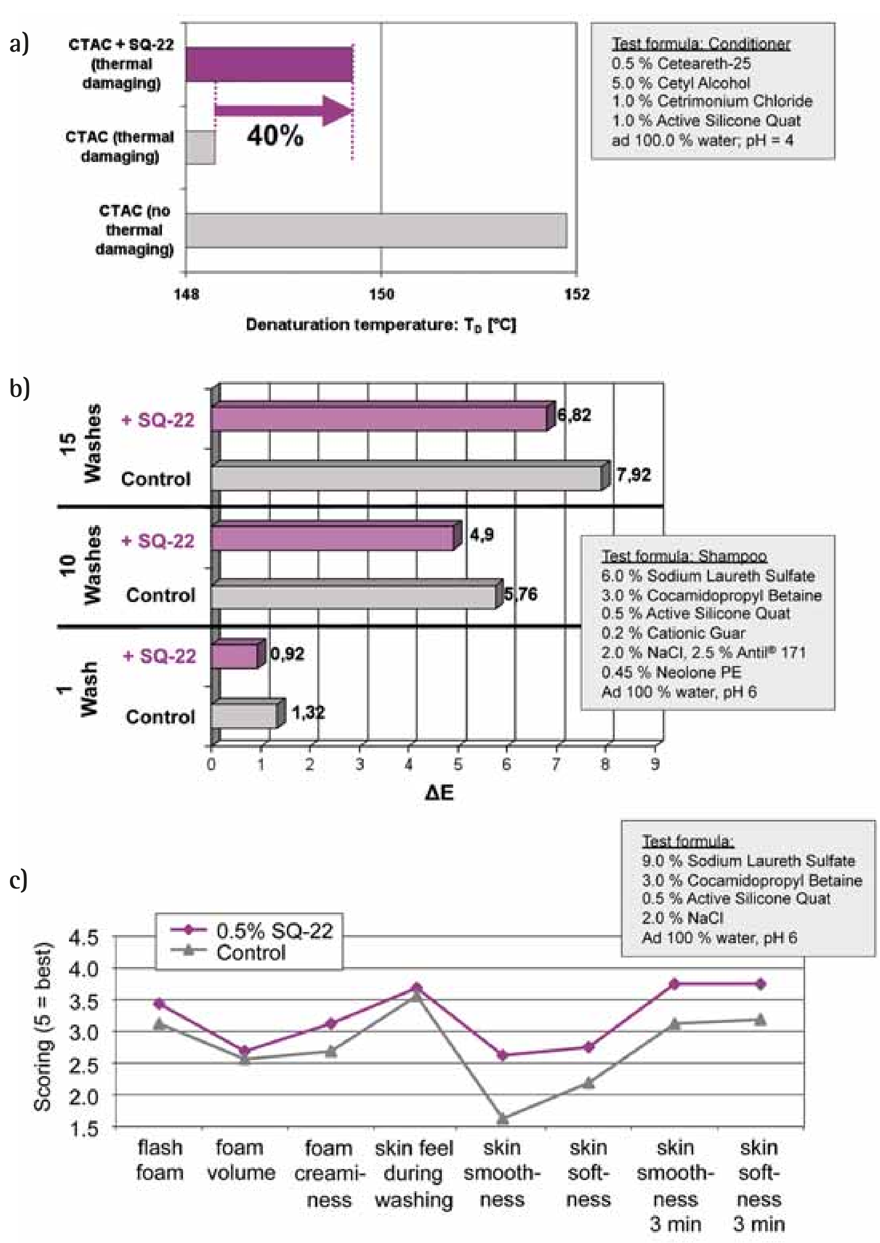

Fig. 4 Silicone Quaternium-22: **a)** Effect on keratin structure of brown undamaged hair as measured by DSC; **b)** Reduced color fading by addition to conditioning rinse; **c)** Sensory effect as assessed via hand wash test

■ Fabric Care

Fabric Softening

Double-chain lipids like lecithin form bilayer aggregates in water; one example being the cell membranes. When dispersed in water, such amphiphiles carrying two alkyl chains form spherically-closed bilayer membranes, so-called vesicles. While vesicles consisting of synthetic lipids are of considerable scientific interest for model membrane studies, it is not widely known that annually more than a million tons of vesicle dispersions are used world-wide: Fabric softeners, which are basically vesicle dispersions of double-chain cationic surfactants. As mentioned already earlier, today these organic quats are based on di- or trialkanolamines and thus carry ester groups between the alkyl chains and the quaternary nitrogen. As a consequence, their biodegradability and hence their environmental profile is acceptable. Needless to say that many fibres, especially cotton, carry some anionic groups on their surface, and therefore fabric softening is done via cationic surfactants. There are several reasons why the customers use fabric softeners. One aspect is the desire for »softness«, but this property is hard to define or to measure, and therefore in the laboratory this property has to be evaluated manually by a trained panel of experts. Another reason for using fabric softeners is definitely the deposition of fragrance onto the textiles, to create the impression of freshness.

Phase Behavior of Fabric Softener Quats

By far most of the softener quat molecules used today carry C18-alkyl chains which are more or less saturated. Therefore, the vesicles are at room temperature in the so called solid-analogue state, i.e. the alkyl chains in the bilayer aggregates are crystallized. Accordingly, in the microscope these vesicles look solid and have sharp edges. Typically, their size in a fabric softener dispersion is in the range of several (up to 20) µm. The analogous quats based on oleic acid, i.e. carrying a double bond in the alkyl chain, can not crystallize and hence their vesicles are in the liquid-analogue state at room temperature. When such dispersions of flexible vesicles are subjected to shear, especially the largest vesicles will break up and hence the particle size distribution is shifted to lower values.

Deposition of Fabric Softener Quats

Depending on the physicochemical properties of the quat vesicles, the location of the quat deposited on the textile will be different, and this will have an influence on the performance. We have studied this aspect already a while ago using fluorescence microscopy (5). In order to visualize the location of the quats on the fabric after the fabric softening step, we have used »glow-in-the-dark« vesicles and fluorescence microscopy. An oil-soluble fluorescence dye has been dissolved in the quat before preparing the vesicle dispersion. Therefore, the dye is only present in the hydrophobic region of the bilayer, and since the water-solubility of the dye is extremely low, the location of the dye indicates the location of the quat. A significant difference between large, solid vesicles **(Fig. 6 a)** and small, flexible vesicles **(Fig. 6 b)** could be detected by looking at the cross-section of a treated cotton fabric: The large, solid vesicles lead to deposition of the quats preferentially at the surface of the fabric, with only little penetration in between the individual fibres of the fabric. In case of the small and flexible vesicles, there is no concentration gradient observable, indicating complete penetration into the fabric. These results correlate very well with the application performance: The »touchable« softness in the case of the large, solid vesicles is much better as compared to the soft vesicles. According to empirical experience, quats carrying saturated alkyl chains lead to better softness than the unsaturated ones. This difference can – at least partially – be explained by the fact that in the case of the solid vesicles, the majority of the quat is located at the surface, i.e. at a location it can be touched. Penetration of the unsaturated quat does have the advantage of better fibre lubrication within the fabric, leading to less wrinkles and less fibre damage. But this effect is at the expense of good feel properties.

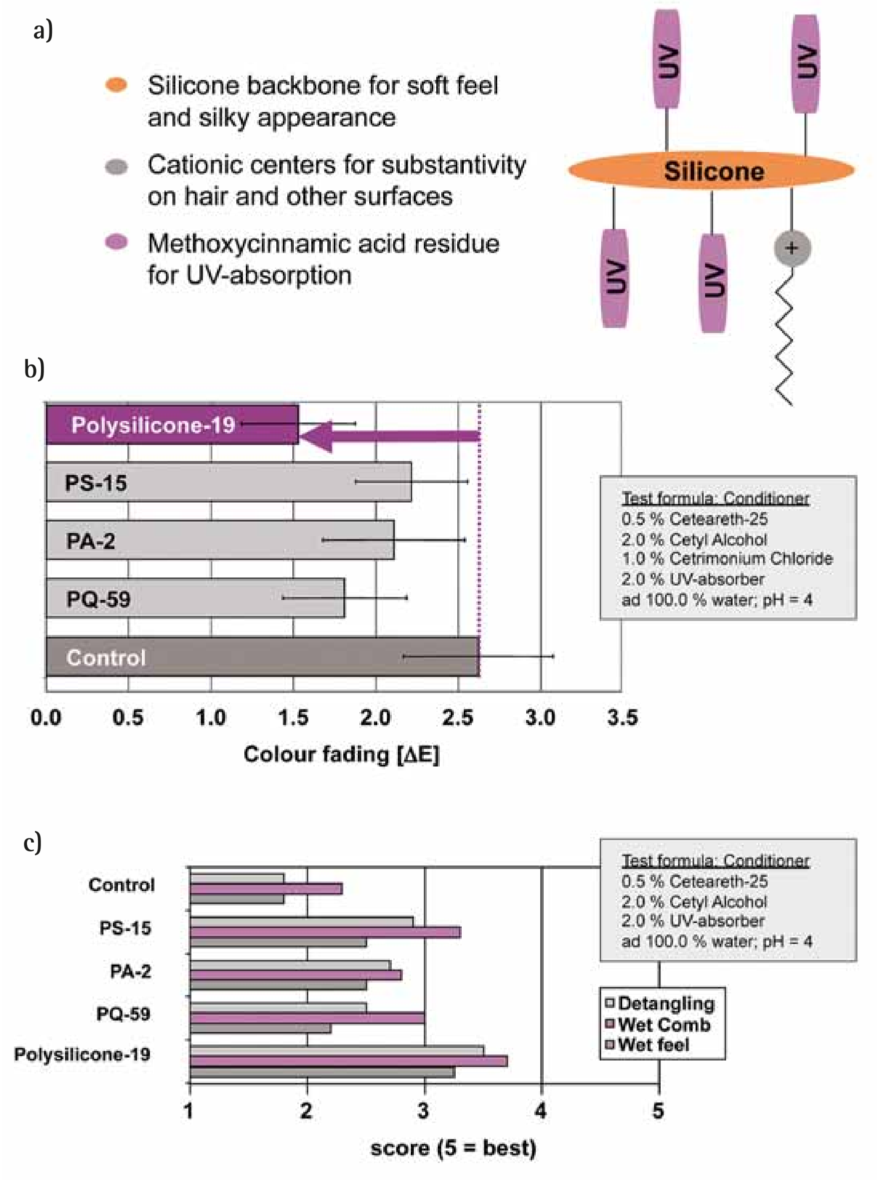

Fig. 5 Polysilicone-19: **a)** Schematic chemical structure; **b)** Reduced color fading by addition of various UV-absorbers to conditioning rinse; **c)** Sensory assessment of conditioning rinses containing UV-absorbers

Effect of Silicone Quats

In order to obtain both good feel and fibre protection, vesicles of saturated quats have been combined with silicone quats **(Fig. 6 c)**. For these experiments, cotton fabric swatches have been treated 30 times, each cycle consisting of washing with a powder detergent containing bleach, rinsing, softening, line drying and ironing. This treatment leads to significant damage of the fabric, as indicated by the reduced tensile strength and the increased elongation at break. The fabric softener containing organic quat with saturated alkyl chains has only limited potential to prevent mechanical damage. This can be easily understood considering the lack of penetration into the fabric. This in turn leads to good softening performance (1. cycle). It can also be seen that increased fibre damage after 30 cycles leads to a lower softness grading, most probably because of increased roughness of the fabric. The addition of silicone quat has positive effects on all three properties measured: The tensile strength turned out to be even higher than of the unwashed control, the elongation is reduced which in turn means better shape retention, and the improvement in softening is quite remarkable. Therefore, it is fair to say that by an appropriate selection of raw materials effects can be obtained which go way beyond simple fabric softening.

a)

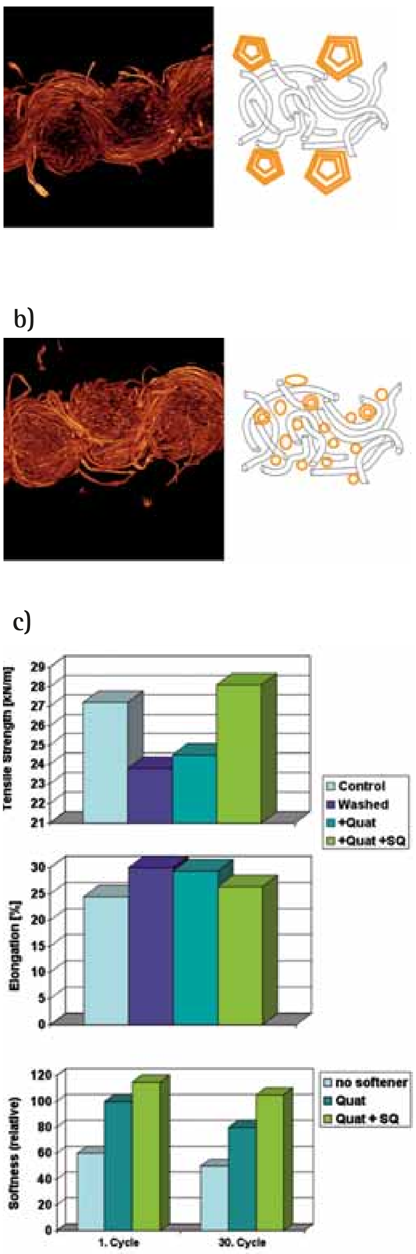

Fig. 6 Fabric softening: **a)** Fluorescence microscopy image of the cross-section of a cotton fabric treated with large, solid quat vesicles containing an oil-soluble fluorescence dye; **b)** Fluorescence microscopy image of the cross-section of a cotton fabric treated with small, flexible quat vesicles containing an oil-soluble fluorescence dye; **c)** Effect of silicone quat on tensile strength, elongation at break and softness of cotton treated 30 times (powder with bleach; softener 17.25% quat + 0.75% silicone quat)

Conclusion

In our daily life, we treat a large variety of surfaces with caring formulations containing cationic surfactants based on oleochemistry and/or silicone chemistry. This is, however, not obvious to most consumers. In this article, the examples of car wash, hair conditioning and fabric softening have been covered, but there are also other interesting topics such as sand-repellent sunscreen formulas based on cationic emulsifiers.

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