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abstract

An innovative, easy-to-clean concept with hydrophilic protective layers formed by functional collagen peptides on cleaned surfaces, has been successfully employed in professional vehicle cleaning applications. This has allowed for the reformulation of cleaners to less alkaline and more environmentally friendly conditions. In addition to improved cleaning results, extended cleaning cycles and reduced water consumption are well documented benefits. Meanwhile these protein protection layers are also finding use in hard-surface cleaners.

Here, the current focus is on effective ready-to-use cleaning products with simplified and reduced cleaning processes even at mild alkaline pH levels. For the first time, the mode of action of these proteins was measured in real-time by means of quartz crystal microbalance experiments. The data suggests that during a cleaning process multiple layers of proteins and surfactants are formed on the surface. These layers create an easy-to-clean effect by repeated application of a cleaning formulation. Even after extensive rinsing with pure water, a compact protein layer remains on the surface which acts as effective barrier against resoiling. The easy-to-clean effect of this protective layer was also confirmed macroscopically with several exemplary household cleaner formulations according to the IKW test-method for all-purpose cleaners on a scrub abrasion and washability tester (TQC Sheen).

Cleaning through a second skin – The role of proteins in a formulation

Many cleaning formulations contain additives for the protection of cleaned surfaces. Most of the surface protectants are based on water-repellant products, like waxes, silicones, and other hydrophobic film forming molecules. The basic design of such products is to leave a cleaned surface in a water-repellant state. This allows water to roll off from the cleaned surface, taking the dirt and soil with it (e.g. waxing a car after washing to obtain a beading effect). However, while this might work well for water-soluble stains, it is very difficult to remove any dispersed water-insoluble compounds once this material has been dried on the water-repellant surface. Furthermore, almost all current surface protectants are based on petrochemical products, which strongly conflicts with the desire of consumers for products with an increased biodegradability and a reduced microplastic footprint.

In order to overcome these challenge, the use of the protein-based additive NOVOTEC® CB800 for surface protection in train cleaning has been described [1-2]. NOVOTEC® CB800 is a concentrated aqueous solution of specific collagen peptides, with an average molecular weight of 3.000 Da and a proline frequency of 14% as well as a hydroxyproline frequency of 13%. When a cleaning formulation is equipped with NOVOTEC® CB800, the polypeptide chains of this natural product will form a protective hydrophilic layer via self-organization during cleaning.

The proposed working mechanism of NOVOTEC® CB800 in combination with cleaners [3] is shown in **Fig. 1**, which represents the cleaning of a train [4]:

First, surfactants are removing soils (step 1). Simultaneously, the protein molecules form a protective layer on the cleaned surface. The protein molecules start to attach themselves to the surface via polar interactions of carboxylic and amino groups within the amino acid chain. A broad range of polar and non-polar side chain-functions assists the protein molecules to form layers on a wide range of surfaces.

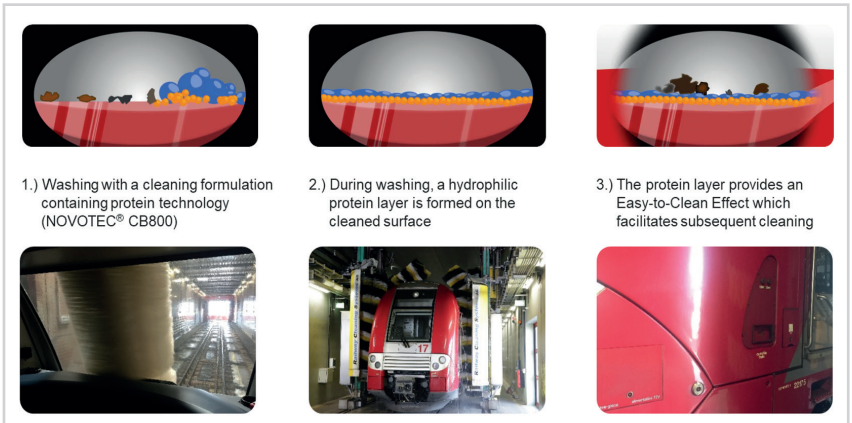

Fig. 1 Scheme of the protective hydrophilic protein layer formation during cleaning of a train surface.

Next, the proteins form a stable network via self-organization (step 2). Polar proteins with a high proline and hydroxyproline content have been found very effective for this purpose. The protein network also incorporates water from the cleaning formulation. On subsequent drying of the surface, the equilibrium moisture content of the protein film typically reaches between 8% and 12% [5].

Once the layer is established, new soil can no longer reach the cleaned surface and either flows along the water bound by the protein film or is removed as the protein layer is dynamically replenished during following cleanings (step 3). As a result, the surfaces are easier to clean.

Luxembourg National Railway Company (CFL) reported a reduction of their washing time by 30%, combined with a reduction of fresh water consumption by 90% after using protein-based cleaners at their facilities [6]. The cleaners were produced by Reinwerk Solutions, located in Bischheim, Germany. A total cost reduction by 50% displayed that the usage of those protein-based cleaners is also commercially attractive [7].

Example of the protein-induced easy-to-clean effect on a glass surface

The easy-to-clean effect caused by the protein protective layers, can be visualized by the following simple experiment: A glass plate was washed with the same glass cleaning base formulation with and without the protein-based additive NOVOTEC® CB800. The left side was prepared without protein, right side with protein (**Fig. 2**, step 1). The composition of the utilized cleaning formulation (including the protein-based additive) is provided in **Tab. 1**.

Afterwards the glass plate was treated with different permanent markers. Next, the glass plate was washed with 40 °C warm water for 30 seconds. On the right side, which was pre-cleaned with the cleaning formulation that included the protein-based additive NOVOTEC® CB800, the markers could be easier washed away (**Fig. 2**, step 2).

Tracking the protein layer formation in real-time

To evaluate the protein-surface interaction during cleaning in more detail, real-time measurements of the experiment mentioned above have been conducted using a quartz crystal microbalance instrument (QCM-D, QSense Analyzer). This equipment can measure the thickness of the protein layer and potential other layers on variable substrate surfaces via change of frequency (thicker layers will reduce the frequency) as well as their viscoelastic properties by detecting the dissipation factor (higher value corresponds to more softness).

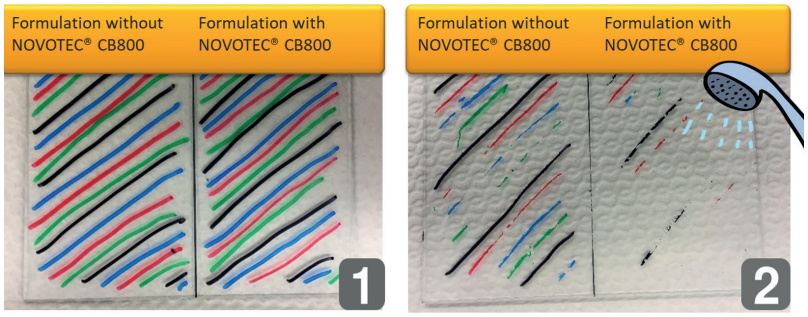

Fig. 2 Glass cleaner with NOVOTEC® CB800 induced easy-to-clean effect
Step 1: Glass plate treated with different permanent markers before rinsing with pure water; Step 2: Glass plate after rinsing with 40 °C warm water.

Glass Window Cleaner (HCI/1001)

Hard Surface Cleaner with a good cleaning an wetting ability. Excellent skin mildness

Phase	Ingredient	INCI	% w/w	Function
A	Deionized water	Water	Qs	
	Carephos® N (ICL)	Sodium Polyphosphate	0.20	Complexing Agent
	GlucoPure® WET (Clariant)	N-C8/10-acyl-N-methyl-glucamin	1.00	Surfactant
	NOVOTEC® CB800 (Gelita AG)	Gelatin Hydrolyzate	2.00	Additive
	Phenoxetol™ (Clariant)	Phenoxyethanol	0.50	Preservative
B	Sodium Hydroxide 10%	Sodium Hydroxide	Qs	pH – Adjuster

Specification:
Appearance: clear liquid
pH-value: 9.20 – 9.80
Viscosity: N/A
Stability test: Stable for 3 months at 4°C, 20°C and 40°C, 1 month at 45°C

Procedure:
I. Mix the components of phase A at room temperature until you have a clear solution.
II. Set pH-value with phase B.

Tab. 1 Glass cleaner with NOVOTEC® CB800 induced easy-to-clean effect.

The QCM-D was equipped with either gold sensors or gold sensors sputtered with soda-lime glass. After equilibrating the sensors with air (step 1, **Fig. 3**) and water (step 2, **Fig. 3**), the glass cleaning formulation equipped with protein as described above (**Tab. 1**) was pumped over the sensor, which resulted in an immediate formation of a relatively soft layer with a calculated thickness of 20-30 nm (step 3, **Fig. 3**). It is hypothesized that this layer consists of the protein layer on the sensor surface and an associated layer of absorbed surfactants. Next, the sensor was taken out of the QCM-D instrument and spin-coated with an ethanol-diluted permanent marker ink (step 4, **Fig. 3**). The ink-soiled sensor was placed back in the QCM-D and the same glass cleaner formulation was pumped over the sensor, but this time without including the protein in the glass cleaner formulation.

The high layer thickness caused by the ink on the soiled sensor vanished within seconds (step 5, **Fig. 3**) and the layer thickness dropped down to almost 5 nm followed by restoring the initial layer thickness of 20 nm. It can be assumed that the ink was washed away together with the associated surfactants from the protein surface at the beginning of step 5 followed by a new surfactant layer formation on the protein surface.

When water was pumped over the sensor, the layer thickness dropped sharply down again to 5 nm level (step 6, **Fig. 3**), as the surfactants were washed away. The dimension of the remaining protein film on the surface did not change on further rinsing with water and stayed on the 5 nm level.

In summary, the QCM-D real-time measurements suggest the following mechanism for the protein-induced easy-to-clean effect:

- Soft multilayers consisting of protein and surfactants are assembled during first cleaning
- Partial dissolving of the layers due to release of surfactants facilitates cleaning
- A thin protein layer remains on the surface as protection layer

Interaction of the proteins with surfactants

In order to better understand the interactions of surfactants with the protein, various combinations of surfactants with

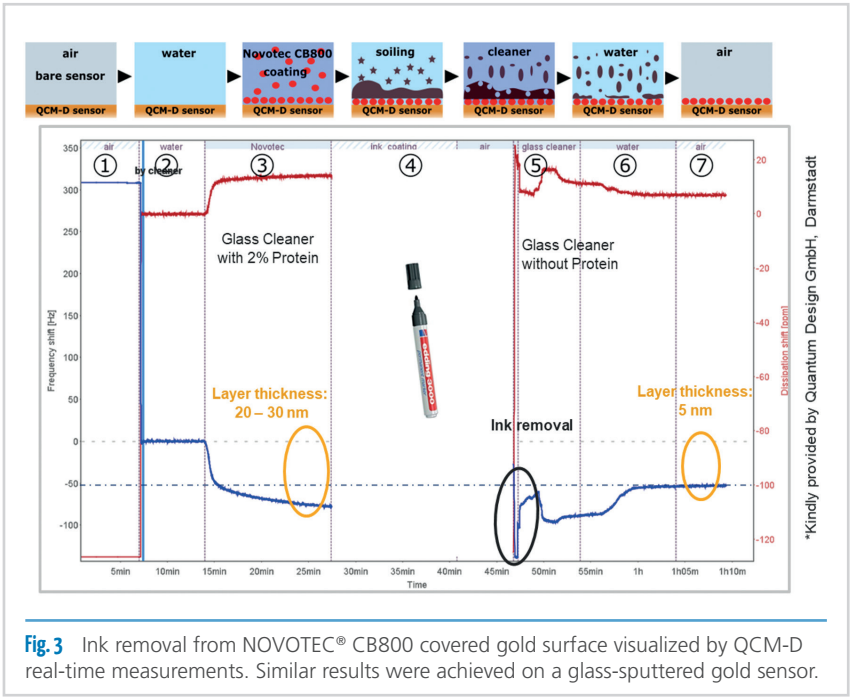

Fig. 3 Ink removal from NOVOTEC® CB800 covered gold surface visualized by QCM-D real-time measurements. Similar results were achieved on a glass-sputtered gold sensor.

NOVOTEC® CB800 have been analyzed regarding their surface tension and contact angle towards cleaned substrates. A previous study [8, 9] included the following surfactants [10, 11]: DODECYLDIMETHYLAMINE OXIDE, SODIUM 2-ETHYLHEXYL IMINO DIPROPIONATE, SODIUM N-LAUROYLSARCOSINATE, SODIUM ETHYLHEXYL SULFATE, SODIUM CAPRYLOYL GLUTAMATE, TIPA-LAURETH SULFATE, N-C8/10-ACYL-N-METHYL-GLUCAMIN, N-C12/14-ACYL-N-METHYL-GLUCAMIN-N-COCO-ACYL-N-METHYL-GLUCAMIN, C10-12 FATTY ALCOHOL EO/PO-ADDUCT, COCO-BETAINE,
COCAMIDOPROPYL BETAINE, ALKYL HYDROXYETHYL DIMETHYL AMMONIUM CHLORIDE, SODIUM LAURETH SULFATE, SODIUM LAURETH SULFATE.
Among all of these surfactants, synergistic interactions – i.e. a lower surface tension with increasing amount of NOVOTEC® CB800 protein – have been observed with glucamin-based surfactants and SODIUM CAPRYLOYL GLUTAMATE; antagonistic results have been found for SODIUM 2-ETHYLHEXYL IMINO DIPROPIONATE. The surface tension of the other surfactants did not change significantly in combination with NOVOTEC® CB800. Concentrations of up to 2.5% protein in a 5% surfactant solution were examined.
The synergistic acting glucamine-based surfactants have been chosen for further analysis of the surfactant-protein interaction during cleaning.

Protein and surfactant concentration and its influence on the cleaning performance

The effect of the surfactant and protein concentration on the cleaning performance was studied by varying the final working dilution of two all-purpose cleaning formulations. One formulation contained NOVOTEC® CB800 and for the other formulation the additive was replaced by water to maintain the amount of the other ingredients (**Tab. 2**). Surface tension and contact angle were determined by optical contact angle measuring and contour analysis system (Dataphysics OCA 50), the reported values are the average of 3 measurements. The cleaning performance was evaluated by using a scrub abrasion and washability tester (TQC Sheen).
For the performance evaluation, the current version of the IKW test-method for all-purpose cleaners [12] was adapted. As studying the protective effect requires protein pretreatment prior to soiling, it was necessary to extend the established IKW test-method by inclusion of an initial cleaning step with the selected formulations. It was decided to simply copy the conditions of the cleaning step for the pre-cleaning.
Following the IKW test-method for all-purpose cleaners, the test soil consisted of 75% peanut oil (Mazola), 23% kaolin and 2% carbon black. The defined test substrate (floor tiles by Villeroy & Boch 3135 30x30cm) was cleaned with ethanol and the test cleaner formulation (5ml) was applied to the surface with the defined towels (Wecovi 02010100, cut to 13x10 cm) by wiping 20 strokes within one minute on a scrub abrasion and washability tester (TQC Sheen). In the next step the test soil was applied on an area of 8x26 cm by screen printing. The soil was burned at 100 °C for 24 h followed by a setting step for 24 h at room temperature. In the final step the tile was again cleaned with the defined towels wetted with 5ml of the test cleaning formulation. This cleaning cycle consisted again of 20 strokes within one minute.
The application of the concentrated cleaner did not show a major difference in the cleaning performance. That was mainly because the cleaner formulation was powerful enough to remove the test soil even without protein pretreatment effectively with 20 strokes (**Fig. 4**). This experiment verified, that the cleaning formulation was adequately formulated to remove the test soil.

Kitchen Cleaner (HCI/1006)
Kitchen Cleaner against grease with an easy to clean effect. Excellent skin mildness.

Phase	Ingredient	INCI	% w/w	Function
A	Deionized water	Water	Qs	
	Carephos® N (ICL)	Sodium Polyphosphate	0.30	Complexing Agent
	GlucoPure® DEG (Clariant)	N-C12/14-acyl-N-methyl-glucamin	2.00	Surfactant
	NOVOTEC® CB800 (Gelita AG)	Gelatin Hydrolyzate	2.00	Additive
	Genaminox® CSL (Clariant)	Coco dimethyl amoneoxide	1.50	Surfactant
	Isopropanol	Isopropanol	1.00	Solubilizer
	Phenoxetol™ (Clariant)	Phenoxyethanol	0.50	Preservative
B	Sodium Hydroxide 10%	Sodium Hydroxide	Qs	pH – Adjuster

Specification:
Appearance: clear liquid
pH-value: 9.50 – 10.00
Viscosity: N/A
Stability test: Stable for 3 months at 4°C, 20°C and 40°C, 1 month at 45°C

Procedure:
I. Mix the components of phase A at room temperature until you have a clear solution.
II. Set pH-value with phase B.

Tab. 2 All-Purpose cleaning formulation with NOVOTEC® CB800 induced easy-to-clean effect.

While the surface tension of both cleaning formulations was almost similar (28.3 and 28.9 mN/m respectively), clear differences were visible regarding the contact angle of the cleaning formulations on a tile washed with ethanol, but without further pretreatment. The protein-based cleaner showed a contact angle of 6.6° while the formulation without NOVOTEC® CB800 had a contact angle of 11.7° (**Fig. 4**). As the surface tension of both cleaners was comparable, the lower contact angle of the protein-based cleaning formulation must be caused by an immediate formation of hydrophilic protein layers once the formulation came in contact with the tile surface.

The impact of the protein protection layers on the cleaning process was clearly visible once the cleaning formulations were diluted with water. The previously mentioned cleaning experiment was repeated, but this time with an aqueous 1:1 dilution of the cleaning formulations (with and without protein) described in **Tab. 2** for the protein based cleaner. Each diluted cleaner was used for the corresponding pre-cleaning and the consecutive cleaning step. The test soil was still effectively removed with 20 strokes from the NOVOTEC® CB800 protection coating, although the pre-cleaning step generating the protein layer was performed with the diluted cleaner. The side of the tile, which was pretreated with the cleaning formulation without NOVOTEC® CB800 remained soiled after 20 strokes (**Fig. 5**).

The analysis of the surface tension and contact angle gave very similar results as received with the non-diluted cleaners. While the surface tension of both cleaners was again almost equal (27.9 and 27.7 mN/m respectively), the contact angle measurement resulted in 4.5° for the protein containing cleaner versus 10° for the protein-free cleaner on a tile washed with ethanol, but without further pretreatment. Thus, obviously even the diluted cleaner was effectively releasing enough protein on the surface of the tile during the first cleaning step, to build a hydrophilic protection layer and make the second cleaning more effective.

In summary, these results are indicating an interesting method for cutting cost of cleaning formulations, especially in applications where cleaners are applied regularly and/or repeatedly.

Differences between cleaning with and without protein protection were also evident at high dilutions (1:5). When the tile was pre-cleaned with the highly diluted cleaning formulations with and without NOVOTEC® CB800, there was still a major difference visible after 20 strokes of the second cleaning step. However, the final cleaning result was not sufficient for both formulations (see **Fig. 6**). This indicates that neither the low protein concentration in the pre-cleaning step nor the surfactant content in the actual cleaning step were sufficient to remove the dirt completely. Interestingly,

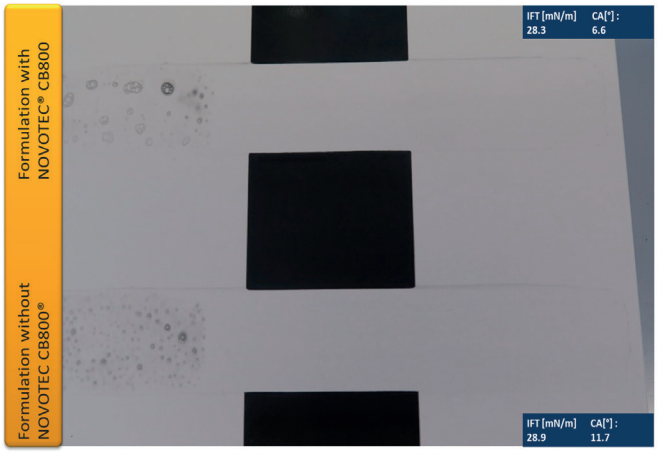

Fig. 4 A tile pre-washed with concentrated cleaner with/without NOVOTEC® CB800 and cleaned again with the respective cleaners shows only a minor improvement due to protein protection of the first cleaning.

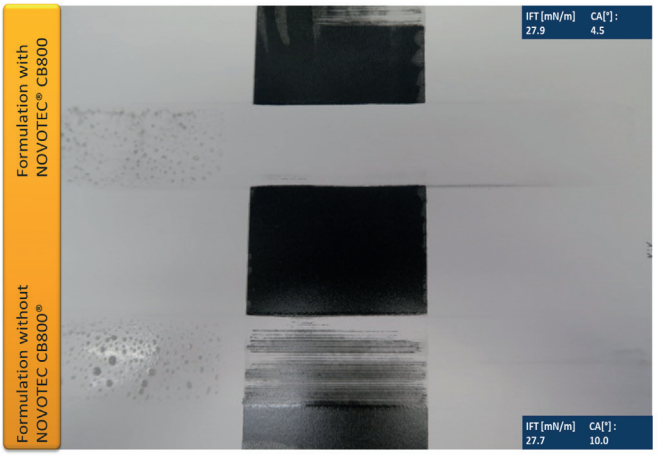

Fig. 5 A tile pre-washed with 1:1 diluted cleaner with/without NOVOTEC® CB800 and cleaned again with the respective cleaners shows a major improvement due to protein protection of the first cleaning.

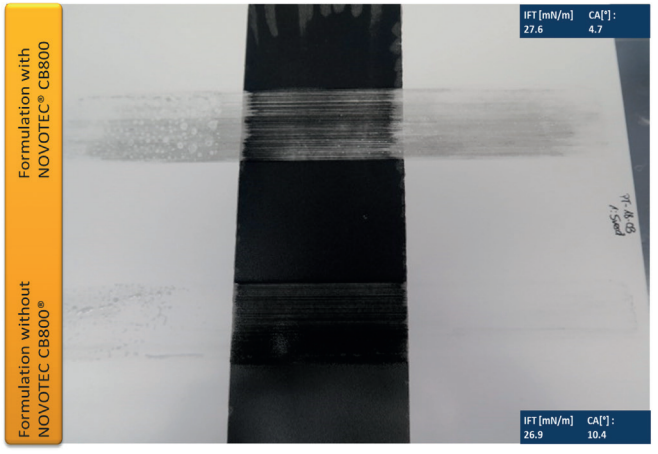

Fig. 6 A tile pre-washed with 1:5 diluted cleaner with/without NOVOTEC® CB800 and cleaned again with the respective cleaners shows only an improvement due to protein protection of the first cleaning but the final cleaning result is not satisfying.

however, the determined contact angle values for the 1:5 diluted cleaners on the untreated tile were quite similar to the values determined for the 1:1 dilutions, which suggests that the hydrophilic protein protective layers are formed even with highly diluted detergent formulations. Thus, the unsatisfactory cleaning result is probably primarily due to an insufficient surfactant concentration.

Conclusion

The presented results show that the performance of water-based cleaners may be boosted by adding small fractions of the protein-based additive NOVOTEC® CB800 to the formulation. During cleaning, the proteins attach themselves to the surface and form stable hydrophilic layers by self-organization. These layers attract water and provide an easy-to-clean effect. Any soil formation on cleaned surfaces can be removed more easily and effectively. QCM-D analyses suggest that if NOVOTEC® CB800 is combined with surfactants, soft multilayers consisting of protein and surfactants are assembled during first cleaning. These layers partially dissolve during subsequent cleaning, releasing surfactants that facilitate the cleaning while a thin protein layer remains.
This opens new opportunities to create more natural cleaners and at the same time provide very cost-effective cleaning formulations by lowering the surfactant concentration.
Moreover, the presented protein-based additive, NOVOTEC® CB800, as a natural polymer, is fully biodegradable, has a very low allergenic potential, protects skin and is not subject of discussions on microplastics in contrast to synthetic polymers.

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