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The Road to More Sustainability and Functionality in Liquid Laundry Detergents

Award

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CFF GmbH & Co. KG

Hydrophobic Cellulose – Micro-fine Texture at Ultra-strong Performance for a Measurable Soft-focus Effect

Solvay

A Natural, Powerful and Biodegradable Suspension Agent for Home Care

SOFW JOURNAL
BEST PAPER AWARD 2021

THANNHAUSEN, GERMANY, 2 DECEMBER 2021

For the second time the SOFW best paper awards winners have been selected. Again, an independent panel of specialists assessed 65 papers published in the SOFW journal in 2021.

Two of the winning papers focus on Home Care, one on Personal Care. We congratulate the winners and encourage everyone in the industry to continue submitting technical and scientific articles. One of our readers from a prominent producer of both Home and Personal Care products recently mentioned, that reading in our trade literature inspires innovations.

Unfortunately, once again the pandemic situation hinders a face to face award ceremony. Never the less we are happy to announce the winners here and sincerely hope, that in 2022 we can all meet in person again.

Congratulations again and: Stay healthy!

The winner of the first prize is the article:

1 The Road to More Sustainability and Functionality in Liquid Laundry Detergents

Authors: A. Phyfferoen, J. Swazey
Companies: CP Kelco UK Ltd. & CP Kelco U.S., Inc.

Abstract: As consumer trends push the laundry markets towards more environmentally friendly formulations and practices, these industries will need an alternative technology to provide reliable suspension. FDC (fermentation-derived cellulose) is a powerful option for both performance and increased sustainability, offering excellent suspension properties, low cost in use, and due to its insolubility, unmatched limits of compatibility. Its three-dimensional net-like structure enables FDC to structure liquids, suspend perfume microbeads at inclusion levels as low as 0.5% - 1.5% "as is", and stabilize opacifiers and any insoluble ingredients with inclusion levels that will depend on the density difference between the media and particle size.

The winner of the second prize is the paper:

2 Hydrophobic Cellulose – Micro-fine Texture at Ultra-strong Performance for a Measurable Soft-focus Effect

Authors: J. Schulte, A. Huneke, J. Ryll
Company: CFF GmbH & Co. KG

Abstract: Cosmetic products for a young and fresh appearance have moved beyond finding their place on the drugstore shelves merely as target group-specific niche products today. They have become established in both day care and colour cosmetics for all age groups. The soft-focus effect, for example, visually reduces small facial wrinkles to make the skin appear rejuvenated within seconds. In the process, fine powders settle into skin imperfections, causing a change in the way light is scattered. CFF GmbH & Co. KG has succeeded in developing an innovative natural raw material that achieves an extraordinary soft-focus effect and keeps up with the performance of synthetic powders such as PMMA and Nylon-12 with its hydrophobic cellulose. Hydrophobic cellulose is on par with any microplastic powders in its sensory properties and texture. It entirely imitates their characteristic profile. This article provides an overview of the application of hydrophobic cellulose as a soft-focus additive in comparison to microplastic powders.

The winning article of the third prize is:

3 A Natural, Powerful and Biodegradable Suspension Agent for Home Care

Authors: S. Zhou, M. Chabert, C. Orizet
Company: Solvay

Abstract: We present an innovative, natural and readily biodegradable suspension agent that opens new possibilities to homecare formulators. When added to detergent formulas, it brings a very powerful suspension capacity without any perceivable impact on viscosity. The agent is based on activated cellulose fibers obtained through the fermentation of starch using specific bacterial strains. We present rheology measurements that allow us to predict the suspension power of a detergent formula supplemented with the agent, based on its rheology at low shear rates. The yield stress value extracted from Bingham plots highly correlates with the density and size of the objects that can be suspended with the agent. We show the application of the agent in multiple home care formulations, in particular the suspension of decorative visual beads and concentrated fragrance in a typical liquid laundry formula. We describe how it is simple to add the suspension agent to a formula due to its pre-activated liquid format. A formula supplemented with the suspension agent is stable for several months at 45°C, with sustained suspension power and no demixion or change in aspect, highlighting the suitability of the suspension agent for commercial consumer products.

The Road to More Sustainability and Functionality In Liquid Laundry Detergents

A. Phyfferoen, J. Swazey

Introduction

When you consider the environmental impact of laundry detergent, it's almost mind-boggling. A 2017 United States Environmental Protection Agency report estimated water usage per load of laundry. The average residential top-loading washing machine can use up to 41 gallons of water per load (155.2 litres). (Newer, more-efficient machines on the market can use as low as 10.5 gallons or just under 40 litres) [1]. Now consider that, globally, 67% of people said they do laundry twice per week, according to a 2017 Nielsen survey. That is a lot of water! Along with the millions and millions of gallons of wastewater, now think about all the laundry detergent being used to clean that laundry and where it ends up. This means extraordinarily large amounts of ingredients derived from petroleum and microplastics entering our waters and potentially harming marine life.

Obviously, if consumers are doing millions of loads of laundry every year, it's because they want clean clothes. So, the market potential for someone who can crack the code of functionality and sustainability is huge. From the consumer's point of view, liquid laundry detergents are easy to dispense, dissolve quickly in cold or hot water, and can even be used to pretreat stains.

Along with functionality, the trend to develop more eco-friendly and biodegradable liquid laundry detergent continues to gain momentum. Liquid laundry detergents and pods now rival powders globally for market share. This presents a challenge, however, of finding suitable ingredients and developing formulations that can provide the performance and experience the consumer expects.
In recent years, companies have innovated the ingredient deck top to bottom with new surfactants, enzymes, brighteners and polymers. Each must be functional in the wash to prevent the redeposition of soil, but also remain stable through the manufacturing process, shelf life and consumer use.

According to Innova Market Insights, ethical-ecological claims ranked second (right behind whitening) for liquid laundry detergent positioning in 2020. Other positioning claims trending across the regions includes paraben-free/hypoallergenic in North America and Asia, pH neutral and antibacterial in Europe, and sensitive skin/hypoallergenic in Latin America [2].

As formulators look to more eco-friendly ingredients, plant-based surfactants have been found to be efficient removers of fat and oil. However, their low viscosity can make finished products appear watered-down. So, companies turned that into an asset by developing more concentrated liquid laundry detergents. Now, as more consumers pursue online buying, concentrated formulas have become a real plus.

Encapsulation Requires Stabilisation

Encapsulation, or the idea of encasing ingredients in a protective "shell" that can be released when needed, has become a dream product for formulators. The technology uses polymers with varying degrees of eco-friendliness, made of polyurethane, polymethyl methacrylate, polylactic acid resins and even formaldehyde. They are designed to open upon dilution in the wash. Fragrances, enzymes and bleaching agents can all be encapsulated to provide added functionality and differentiation for laundry detergent.

In liquid laundry detergents, encapsulated decorative beads and opacifiers require suspension and stabilization. Using nature-based solutions to achieve this has previously been problematic. It is especially difficult in highly concentrated surfactant systems due to compatibility limitations and the need to avoid adversely affecting the viscosity and pour properties of the product.

With more countries imposing environment-related regulations around detergent ingredients, biodegradability becomes just as important as being nature-based. Options to replace petroleum-derived materials with those derived from sustainable sources such as crops already exist in the market. Although a partial solution, it still doesn't address a product's chemistry, which may not be biodegradable in our water systems. For example, using ethylene-derived polymers may help a company avoid the use of petroleum resources, but the final product may still not be biodegradable. Mineral-based opacifiers offer great promise in this area as an environmental option but do not self-suspend and require help with stability.

So, we see the need for stabilisation in the liquid matrix is key. A wide range of nature-based suspension aids can be considered (e.g., xanthan gum, carrageenan, various cellulose-ethers, as well as natural clays) but there are limitations to their use. Xanthan gum, for example, can provide excellent suspension in surfactant-based, personal care formulations but it cannot recreate the overall rheology that is generally preferred, and that people are used to, due to its high pseudoplasticity. In addition, the use of salt-induced surfactant thickening, in combination with xanthan gum or most other biodegradable viscosity modifiers, often leads to unsightly hazing. There are also limits to how concentrated the products can be before these water-soluble, nature-based products start to precipitate out of solution and cause phase separation.

In recent years, the trend to improve the fragrance and whitening experience in laundry care has been evolving – from increasing the loading of fragrance to the inclusion of encapsulated polymers. Today, the challenge remains to sustainably suspend them. There is a critical need for a new, nature-based suspension aid that provides

- Excellent biodegradability
- Reliable performance
- Low cost-in-use
- Compatibility with high surfactant and surfactant-thickened formulations
- The ability to provide suspension properties without adversely affecting pour viscosity

FDC, a Nature-Based and Biodegradable Technology

A case can be made for fermentation-derived cellulose. Cellulose is common in nature. Chemically identical to plant-derived cellulose, fermentation-derived cellulose is a unique and readily available form, which offers properties not possible with other sources of cellulose. As a consequence of being produced through fermentation, the cellulose fibers possess a very fine diameter and exist as a three-dimensional, highly reticulated, net-like structure that gives a very high surface area-to-weight ratio. This three-dimensional, net-like structure allows the FDC to create a true yield value at low concentrations in a formulation, even those with little or no water, and so provide a mechanism for reliable structuring of liquids and stabilization of components with minimal or no impact on the finished product's viscosity and dispersibility. The best part: When the product washes down the drain, it easily biodegrades.

In addition, as it is not water soluble:

- FDC's performance does not depend on the water content of the system it is added to
- FDC does not thicken or add to the perceived viscosity at the typical use levels used for suspension
- FDC is compatible with high levels of salts and surfactants that would cause most water-soluble polymers to precipitate.
- FDC is insensitive to many factors impacting water-soluble polymers such as temperature, shear, salt, pH, but also it is far less susceptible to acids, bases, oxidizers and reducing agents, as these cannot attack the individual linkage points as readily as when polymers are fully solubilized.
- FDC is much less susceptible to cellulase enzyme degradation compared to water-soluble cellulose derivatives (e.g., CMC, HEC, etc.) thanks to its insoluble nature and net-like structure making any enzyme degradation much slower to manifest.

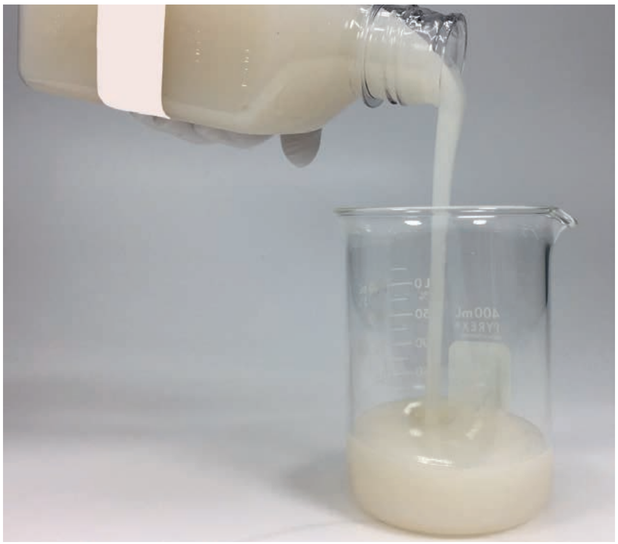

Fig. 1 Fermentation-Derived Cellulose comes ready to use and does not require pH adjustment or high shear mixing to be functional. Use levels range from 0.5% to 5% depending on the formulation and what is to be stabilized.

How Should Fermentation-Derived Cellulose Be Used?

Yield stress is a measure of the force required to initiate flow in a gel-like system. FDC is effective at creating a true yield stress allowing particles to be suspended indefinitely, so long as the force (stress) required to suspend them is less than the yield stress developed by the FDC network. Very low concentrations of FDC are also needed in the formulation to create yield stress, making it an affordable suspension aid that does not disturb pour viscosity of the final product. In essence, the suspension properties of FDC are largely decoupled from viscosity effects. Formulations can be designed that range from water-thin to honey thick. FDC's high compatibility with salt-induced surfactant thickening is also unique among nature-based polymers.

In summary, the unique yield stress properties imparted by FDC can provide excellent stability to a wide variety of surfactant-based formulations. These formulations can be highly concentrated (from typically 5% to 45%) and even some pure surfactant and non-aqueous formulations are possible.

In the manufacture of many surfactant-based laundry products, it is often convenient to add FDC as one of the last ingredients. Once added, it will quickly begin providing suspen-

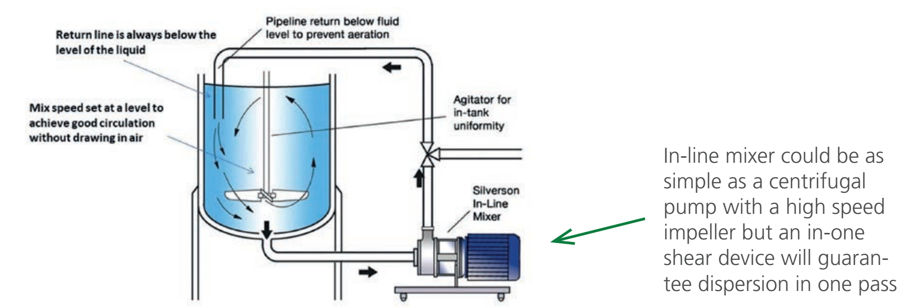

Fig. 2 Optimal mix design to disperse Fermentation-Derived Cellulose while preventing air incorporation (Graphic source: Silverson Machines, Inc.: used with permission).

sion capabilities to the formulation and care may be required to avoid trapping air bubbles. One way of achieving efficient dispersion of the FDC and prevention of air is to use an inline mixer with a recirculating line like the one shown below in **Figure 2**.

In this way, FDC can be incorporated very gently into the bulk mixing tank to prevent air but as it passes through the inline mixer, full dispersion of the FDC is achieved very rapidly. If the inline mixer is of a rotor-stator design, one pass may be enough for full dispersion and maximum yield stress.

FDC, Unprecedent Liquid Structuring and Particle Suspension

Fermentation-Derived Cellulose can provide stability at very low concentrations, which has a wide range of benefits in addition to cost in use and sustainability. In some systems, approximately 3% of the readily dispersible, activated FDC can achieve yield stress values of around 0.7-1.5 Pascal (measured using static yield stress techniques) depending on the formulation. The yield stress increases with use level at a factor of about 1.5. The yield stress triples as the FDC concentration doubles.

In some liquid laundry systems, concentrations below 1% generated sufficient yield stress to give long term stability of encapsulated fragrances. The yield value required will depend upon what is being suspended but most fragrance encapsulates and pearlescents can usually be stabilized with a yield stress of less than 0.1 Pa. Most decorative beads can be suspended with a yield stress of 0.6 to 1 Pa. Opacifiers, depending on their concentration, size, and density may be stabilized with as low as 0.5% FDC. These low-in-use concentrations allow FDC to be used in formulations where transparency is required.

Identifying which grade is best for any given formulation is a relatively simple process: the best grade is that which gives the highest yield stress at any given concentration and under the mix conditions available. If proper dispersion was attained, the yield stress should not significantly change if mixed under strong mixing conditions. The yield value should be stable or modestly increasing with time. Once the best grade is identified, its concentration can be optimized. This article focuses heavily on the application of FDC in laundry and homecare products, but its valuable properties will also make it useful in a wide variety of related applications and formulations, providing good suspension at very low use levels and without creating high pour viscosity.

Conclusion

As consumer trends push the laundry markets towards more environmentally friendly formulations and practices, these industries will need an alternative technology to provide reliable suspension. FDC is a powerful option for both performance and increased sustainability, offering excellent suspension properties, low cost in use, and due to its insolubility, unmatched limits of compatibility. Its three-dimensional net-like structure enables FDC to structure liquids, suspend perfume microbeads at inclusion levels as low as 0.5%-1.5% "as is", and stabilize opacifiers and any insoluble ingredients with inclusion levels that will depend on the density difference between the media and particle size.

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[1] EPA WaterSense Water Efficiency Management Guide, Residential Kitchen and Laundry, 2017. https://www.epa.gov/sites/production/files/2017-10/documents/ws-commercial-buildings-waterscore-residential-kitchen-laundry-guide.pdf, last cited 02.21.21.

[2] Innova Market Insights, Laundry Detergent – Liquid Gel Subcategory Report, H1 2020.

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Hydrophobic Cellulose – Micro-fine Texture at Ultra-strong Performance for a Measurable Soft-focus Effect

J. Schulte, A. Huneke, J. Ryll

abstract

Cosmetic products for a young and fresh appearance have moved beyond finding their place on the drugstore shelves merely as target group-specific niche products today. They have become established in both day care and colour cosmetics for all age groups. The soft-focus effect, for example, visually reduces small facial wrinkles to make the skin appear rejuvenated within seconds. In the process, fine powders settle into skin imperfections, causing a change in the way light is scattered. CFF GmbH & Co. KG has succeeded in developing an innovative natural raw material that achieves an extraordinary soft-focus effect and keeps up with the performance of synthetic powders such as PMMA and Nylon-12 with its hydrophobic cellulose. Hydrophobic cellulose is on par with any microplastic powders in its sensory properties and texture. It entirely imitates their characteristic profile. This article provides an overview of the application of hydrophobic cellulose as a soft-focus additive in comparison to microplastic powders.

Introduction

Aging skin loses elasticity and tone. Skin becomes thinner and drier as it matures. With the appearance of fine wrinkles, the skin begins to look uneven and less fresh. Women over the age of 35 find the changing appearance of their skin disturbing. Their desire for a flawless and rejuvenated appearance is moving increasingly to the focus.

As a consequence, the sales volumes of anti-aging products are increasing every year. The customer range has expanded considerably in terms of the age and gender of the buyers as more and more men have started using anti-wrinkle creams as well as women.

In addition to conventional anti-aging care based on active substances, visual techniques are used in day care or make-up to make the skin look rejuvenated. The principle of the soft-focus effect places fine particles in the skin folds that make incident light scatter less. Wrinkles appear reduced, making the skin look fresher and more youthful. The soft-focus effect is used in both skincare and colour cosmetics for teint products aimed at visually smoothing the skin and concealing wrinkles.

CFF GmbH & Co. KG has developed a new ingredient for an excellent soft-focus effect. Its hydrophobic cellulose is produced from plant-based raw materials such as wood or bamboo. Natural cellulose has already proven its worth for a refined skin feeling in skin care repeatedly. Cellulose stands out for its high water- and oil-binding capacity. This makes formulations appear less sticky and has them absorbed more quickly by the skin. With its innovative hydrophobic processing, CFF GmbH & Co. KG has succeeded in specifically optimising the function of natural plant fibres using a gentle process.

The novel hydrophobic cellulose achieves an excellent soft-focus effect while being able to imitate the characteristic skin feel of fine microplastic powders such as polymethyl methacrylate (PMMA) and nylon. In spite of widespread reporting on the subject of microplastics, these continue to be used for sensory optimisation of creams and visual softening of skin imperfections.

This article explains how hydrophobic cellulose can perfectly mimic the special properties of microplastic powders based on plant-based and biodegradable raw materials.

Texture additives for the soft-focus effect

Soft-focus technology is an important part of current anti-aging skin care, using the simplest laws of physics for its effect. The term of "soft-focus" refers to the visual concealment of small wrinkles and lines by selective control of the transmission and scattering of light into and from the skin. Skin irregularities are visually perceived by their high contrasts **(Fig. 1)**. Fine texture additives settle in the skin wrinkles and act as a soft focus there. Contrast is visually reduced and irregularities on the skin surface seem to disappear. The advantage of this method over active-substance-based anti-aging care is that it can be perceived immediately after application. As soon as it is applied, the formulation makes the skin appear more even and rejuvenates the complexion to appear velvety and fresh. Synthetic particles such as Nylon-12 and PMMA with specific particle sizes below 1-12 µm, continue to be used for the soft-focus effect. In addition to the soft-focus effect itself, they are also said to improve feel and add a matting effect. Although some natural alternatives are already available on the market, only few show an adequate, convincing performance.

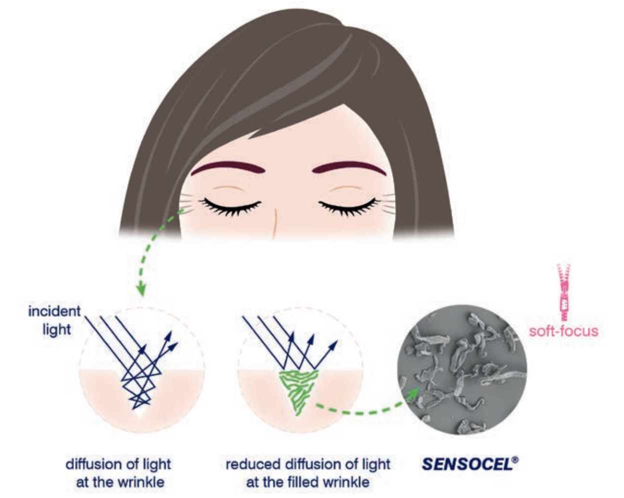

Fig. 1 Graphical representation of the soft-focus effect with SENSOCEL®: *Bottom left detail: without application of a texture additive, light scattering in skin wrinkles is not compensated. The skin looks slack and tired. Young, healthy skin can reflect the incoming light better. Use of texture additives with a soft-focus effect (bottom centre detail) reduces scattering to improve skin appearance. Bottom right detail: natural, biodegradable cellulose particles from CFF GmbH & Co. KG*

The latest development from CFF GmbH & Co. KG uses hydrophobic celluloses that are in no aspect inferior to the performance of plastic powders such as Nylon-12 and PMMA. In addition to an excellent soft-focus, the hydrophobic SENSOCEL® 5+ (1-7 µm) and SENSOCEL® bc 20+ (20 µm) cellulose powders give modern skin care products and colour cosmetics a soft finish and stand out positively with their natural origin.

Innovation: Hydrophobic Cellulose

Natural cellulose serves as a tried and tested additive to positively influence sensory properties and texture in order to make skin-care products and colour cosmetics less glossy and sticky, powdery, and faster absorbed. Natural hydrophobic cellulose combines all of these properties with an even more exclusive, very powdery skin feel.

CFF GmbH & Co. KG has developed a special production process for its production of hydrophobic cellulose to allow individual control of the degree of hydrophobisation. Turning cellulose hydrophobic optimises its function and feel alike. SENSOCEL® 5+ and SENSOCEL® bc 20+ produce cosmetic formulations with very soft and even, skin-friendly textures – properties with positive effects in particular in loose and pressed powders. Flow properties have been optimised as well to permit easy use in body powders.

Hydrophobic celluloses offer outstanding performance in emulsions. Even small amounts achieve an exclusive, very light, homogeneous, and smooth texture. The new hydrophobic plant fibres can be stabilised easily even in formulations with low viscosity. They offer a high overall process stability.

These newly developed characteristics turn hydrophobic cellulose into a natural alternative to microplastic powders such as polymethyl methacrylate (PMMA) or Nylon-12.

Background Information on Microplastics

By banning microplastics in rinse-off products, the EU and many other countries have taken a significant step towards making the future more environmentally friendly. Developments following this regulation clearly reflect that there are natural alternatives that can replace microplastic beads in rinse-off products. The next essential step will be a ban on microplastic particles from fine microplastic powders characterised by an even smaller particle size and used in leave-on products that are not covered by the current one yet. The particularly fine synthetic powders PMMA and Nylon-12 continue to be considered important texturisers and sensory enhancers in skin-care products and colour cosmetics. Many of the plastic powders are barely – or not at all – biodegradable.

Biodegradability

Biodegradability describes the process of decomposition of organic material by microorganisms, such as fungi and bacteria, into nutrients that are either used to produce energy for the microorganisms or returned to the environment. Biodegradation is a process of self-purification in surface waters and used specifically to purify wastewater in sewage treatment plants. Various methods for determining biodegradability are known. In cosmetics, the OECD guidelines for testing chemicals have become established. Based on them, biodegradability of readily biodegradable substances is usually determined in an aquatic environment under aerobic conditions in accordance with OECD 301. Substances with limited biodegradability are analysed based on OECD 302 and considered basically or inherently biodegradable. The OECD 302 tests are performed in activated sludge. Special degradability tests such as OECD 311, run in anaerobic conditions, also determine biodegradation in digested sludge. However, a large share of microplastic reaches the sea via runoff and particle-size-related passage through sewage treatment plants and remains in the water there for long periods. This highlights the importance of testing biodegradability under freshwater conditions.

The test method recommended to determine biodegradability of natural polymers is EN ISO 14851:2019. It determines full biodegradation in a closed respirometer by measuring the oxygen demand in an aqueous medium. As a consequence, determination of biodegradability in accordance with EN ISO 14851:2019 simulates a highly realistic sea environment.

Biodegradability of hydrophobic cellulose has been determined using EN ISO 14851:2019. It came out at 71% after 44 days. Both Nylon-12 and PMMA, used for comparison with hydrophobic cellulose for all the tests described in this article, are classified as non-biodegradable.

Measurement of Light Deviation by Colorimetric Analysis

Colour measurements were performed on the skin and evaluated in order to compare the soft-focus effect of different texture additives. A Minolta Spectrophotometer CM-3500 from Konica Minolta was used for the colour measurements. Its results were evaluated using the CIELAB colour space. The hydrophobic celluloses SENSOCEL® 5+ and SENSOCEL® bc 20+, PMMA, and Nylon-12 were the texture additives chosen for analysis and comparison to each other.

Colorimetric Measurements in the Pure Substance

The first measurement took place with the pure substance on cleansed, dry skin. 1 mg/cm² of product was applied to the skin respectively. Following this, luminance L* **(Fig. 2)** was measured. The results make it clear that all analysed texture additives positively affect luminance value to make the skin appear brighter. The hydrophobic cellulose SENSOCEL® 5+ and polyamide powder Nylon-12 influenced skin brightness most strongly in the test.

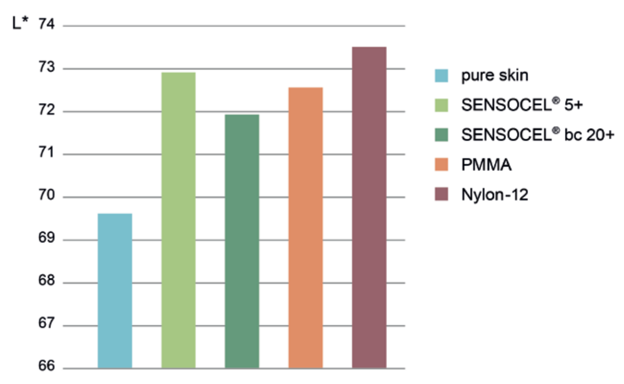

Fig.2 Measurement results for the L* value as a powder on the skin

Colorimetric Measurements in Polyacrylate Gels

In the next step, the light-scattering influence of the in a neutral water-based gel (0.5% acrylate polymer) were measured by incorporating the texture additives into the gel at 2% each. Then, 6 mg/cm² of each gel were applied to the cleansed, dry skin. Each texture additive was subjected to 15 colour measurements from which a mean value was calculated **(Table 1)**.

The results show a positive effect on the luminance value in both hydrophobic celluloses. The colour differences ΔE were determined to be between 1.0 and 3.0. This reflects visible to significant colour differences. In particular, the values of the gel with 2% SENSOCEL® 5+ show that use of hydrophobic cellulose improves the appearance of the skin almost to the same degree as Nylon-12.

Sample	L*	a*	b*	ΔE
Standard gel	69.00	6.30	14.39	
Gel with 2% SENSOCEL® 5+	70.12	7.27	12.87	2.122
Gel with 2% SENSOCEL® bc 20+	69.68	6.95	12.92	1.738
Gel with 2% PMMA	69.30	6.88	13.28	1.440
Gel with 2% Nylon-12	70.64	6.04	12.99	2.167

Tab. 1 Results of colorimetric analysis in a polyacrylate gel.

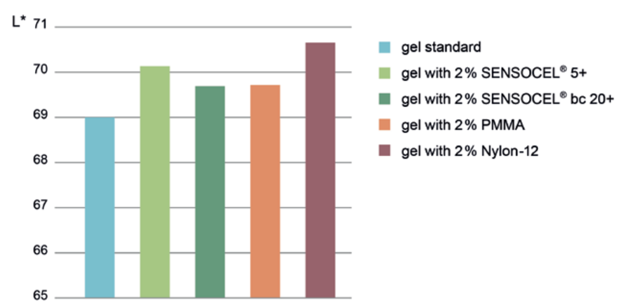

Fig.3 Luminance L* results of texture additives in a polyacrylate gel

Figure 3 graphically supplements the luminance results in the gel. With a luminance value of 70.12, SENSOCEL® 5+ achieves values that are comparable to those of Nylon-12. Both hydrophobic celluloses make the skin appear lighter and reach similar luminance values in the test that are in the same order as those of the microplastic powders used in the experiment. SENSOCEL® 5+ even achieves a greater luminance than PMMA. SENSOCEL® 5+ and SENSOCEL® bc 20+ are suitable for reproducing the soft-focus effect of PMMA or Nylon-12 and for making the teint look fresher without compromising performance while using only ingredients based on natural raw materials.

Visual Comparison of the Soft-Focus Effect

The skin area used for the measurement was analysed after application of the respective gels with the different texture additives as well as with a standard additive-free gel (reference sample) **(Fig. 4)**. The skin area with the standard gel (4a) shows distinct wrinkling as compared to the gels with texture additives (4b-4e). The skin imperfections create a greater contrast in the standard gel, making the skin look older, while all gels with hydrophobic cellulose and microplastic show a soft-focus effect. The difference in luminance for hydrophobic celluloses (4b and 4c) compared to PMMA (4d) is not visually distinguishable, which supports the measured data.

Sensory Effect

The sensory parameters of "matting", "powderiness", "heavy skin feeling", "stickiness", and "softness" were to be assessed.

Matting describes how matte or glossy the skin appears after the cream is applied and then absorbed. Powderiness determines how dry (powdered) the skin feels after application. Regarding a heavy feeling on the skin, the subjects were asked to compare whether one of the formulations weighed the skin down more than the other. Stickiness and softness refer to the feel of the skin right after application.

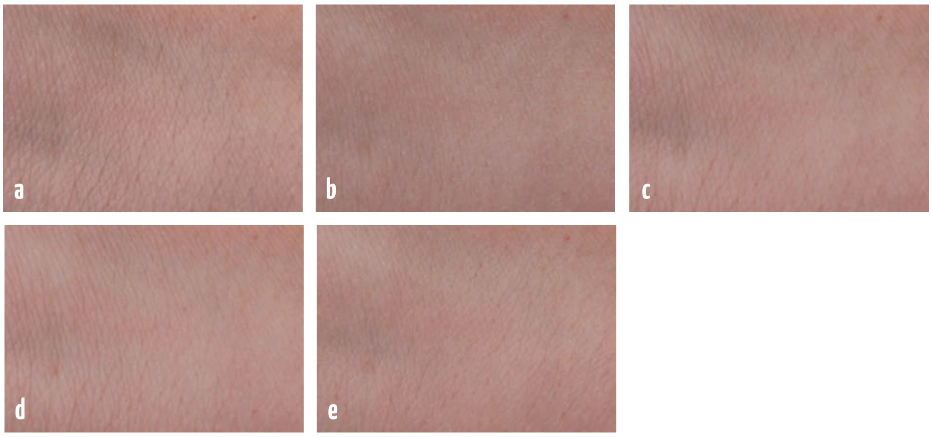

Fig. 4 Photographs of the wrist after application of gels with different texture additives *(a: Standard, b: SENSOCEL® 5+, c: SENSOCEL® bc 20+, d: PMMA, e: Nylon-12)*

Texture

In the evaluation of texture, "homogeneity", "spreadability", "absorption", and "greasiness" were defined as parameters to be evaluated. Homogeneity determines how homogeneous the formulation itself appears. Spreadability describes how easy the formulations were to spread on the skin. Absorption refers to how quickly the formulations were absorbed by the skin. Greasiness means the extent to which the formulations feel greasy when spreading them. The subjects were asked to compare the performance of SENSOCEL® 5+ with that of PMMA and that of SENSOCEL® bc 20+ with that of Nylon-12. This comparison was chosen on purpose because the particle sizes of the two texture additives to be compared respectively are similar.

Sensory Assessment – Comparison of Sensory Effect & Texture

The comparative test was meant to determine whether hydrophobic cellulose can reproduce the sensory and textural properties that are typical for microplastics.

Hydrophobic cellulose powders were evaluated for sensory effects and texture in direct comparison to PMMA and Nylon-12 in a face cream. The blind test comprised 39 subjects. One quarter of the subjects were male and three quarters were female, with 65% of the subjects being older than 30 years.

A face cream with 3% texture additive each **(Table 2)** was used as the formulation.

Ingredient	INCI	Supplier	Quantity [%]
Water phase	**Temperature 80°C**		
Water, demineralised	Aqua		71.70
Glycerine 99.5%	Glycerine		5.00
Fat phase	**Temperature 80°C**		
Cetiol SB 45	Butyrospermum Parkii (Shea) Butter	BASF	1.00
Montanov 68	Cetearyl Alcohol, Cetearyl Glucoside	Seppic	5.00
Myritol 318	Caprylic/Capric Triglyceride	BASF	8.00
Olive oil, cold pressed, organic	Olea Europaea (Olive) Fruit Oil	Gustav Heess	1.00
Extra phase	**Temperature 25°C**		
Hydrolite 5	Pentylene Glycol	Symrise	5.00
SENSOCEL® 5+ / SENSOCEL® bc 20+ / PMMA / Nylon-12			3.00
Perfume phase	**Temperature 25°C**		
Cotton Water	Perfume	Cosnaderm	0.30
Total			**100.00**

Tab. 2 Face cream formulation with 3% texture additive

The face cream with SENSOCEL® bc 20+ was found to be nearly as soft as the formulation containing Nylon-12 **(Fig. 5)**. In the criteria of "stickiness" and "heaviness on the skin", SENSOCEL® bc 20+ was judged to be very slightly stickier and heavier. In terms of "powderiness" and "matting", SENSOCEL® bc 20+ exceeds the rating of Nylon-12. SENSOCEL® bc 20+ has a convincing result in the "texture" test, as test subjects rate it as more homogeneous and easier to distribute. The high water-binding capacity of SENSOCEL® bc 20+ (3.15 g water/g) as compared to Nylon-12 (1.9 g water/g) noticeably affects the "absorption" parameter. Test subjects reported quick development of a dry skin feeling. Where greasiness is concerned, the formulation with SENSOCEL® bc 20+ also keeps up with the one containing Nylon-12. More than half of the test subjects would prefer the SENSOCEL® bc 20+ after direct comparison

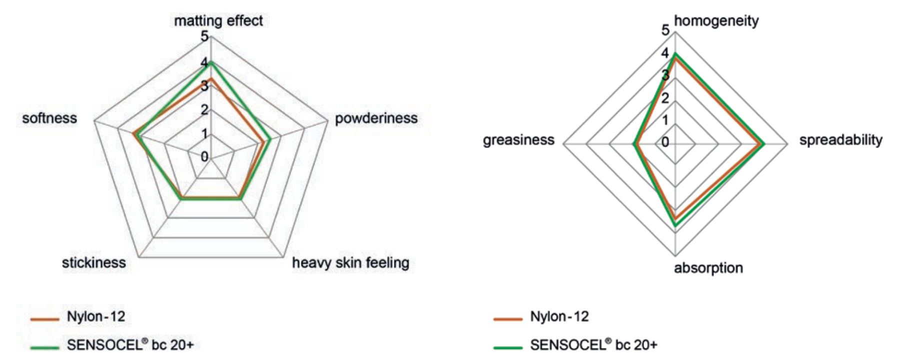

Fig. 5 Evaluation of the test with SENSOCEL® bc 20+ vs. Nylon-12 *(sensory on the left, texture on the right)*

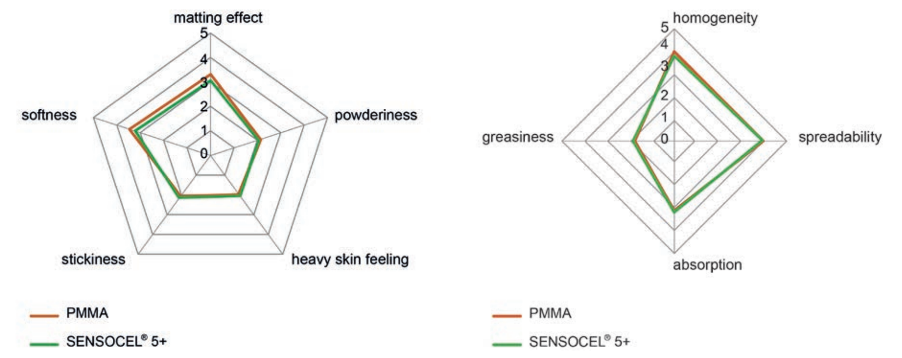

Fig. 6 Evaluation of the test of SENSOCEL® 5+ vs. PMMA *(sensory on the left, texture on the right)*

Test subjects come to similar results when comparing SENSOCEL® 5+ to PMMA **(Fig. 6)**. SENSOCEL® 5+ has a high performance that is comparable to PMMA in terms of its sensory properties. SENSOCEL® 5+ adequately simulates the characteristic texture produced by PMMA. In the direct selection, 67% of the test subjects chose the option with the synthetic powder PMMA.

Result

Use of texture additives with a soft-focus effect reduces light diffusion and improves skin appearance. The latest development by CFF GmbH & Co. KG has resulted in the innovative hydrophobic celluloses SENSOCEL® 5+ and SENSOCEL® bc 20+ that offer some natural, biodegradable alternatives in leave-on products.

Both hydrophobic celluloses positively affect the luminance value (ΔE) with an adequate effect when compared to the widely used plastic-based texture additives PMMA and Nylon-12, respectively, reaching between 1.0 and 3.0 in the pure substance and in a water-based polyacrylate gel. This change ΔE can be described as a visible to significant change in light scattering. SENSOCEL® is a fully plant-based method for eliminating microplastic powders from skin care products in the future, further reducing the amount of microplastics that enter the environment.

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A Natural, Powerful and Biodegradable Suspension Agent for Home Care

S. Zhou, M. Chabert, C. Orizet

abstract

We present an innovative, natural and readily biodegradable suspension agent that opens new possibilities to homecare formulators. When added to detergent formulas, it brings a very powerful suspension capacity without any perceivable impact on viscosity. The agent is based on activated cellulose fibers obtained through the fermentation of starch using specific bacterial strains. We present rheology measurements that allow us to predict the suspension power of a detergent formula supplemented with the agent, based on its rheology at low shear rates. The yield stress value extracted from Bingham plots highly correlates with the density and size of the objects that can be suspended with the agent. We show the application of the agent in multiple home care formulations, in particular the suspension of decorative visual beads and concentrated fragrance in a typical liquid laundry formula. We describe how it is simple to add the suspension agent to a formula due to its pre-activated liquid format. A formula supplemented with the suspension agent is stable for several months at 45°C, with sustained suspension power and no demixion or change in aspect, highlighting the suitability of the suspension agent for commercial consumer products.

Introduction

Recent years have seen a dramatic shift in consumer expectations towards more ecofriendly, and natural homecare products, yet with maintained or improved performance versus existing formula. Also, the increasingly stringent regulations (e.g. microplastics in Europe) that will come into force in the near future are pushing the specialty chemicals industry to seek innovative solutions to equal the high performance of existing synthetic polymers with sustainable and natural alternatives. In addition to the massive ecoprofile improvement needed for home care polymers, an ever more competitive environment also calls for more differentiation and premiumization of brands serving the western market.

The suspension agent presented in this paper is an attempt to answer these two needs. On the one hand, it is a 100% natural, readily biodegradable cellulose-based product obtained by the fermentation of starch by a carefully selected, non-genetically modified bacterial strain. On the other hand, this product brings new features to the table when added to detergent formula by imparting a powerful suspension capacity with no impact on apparent flow viscosity. This allows home care product formulators to offer new, differentiating features to products and to consumers.

First, we introduce the product and its manufacturing process, together with some typical detergent formula used in this paper, as well as the methods needed to characterize the formulations. We then present rheological measurements designed to control the quality of the finished product. Our rheology method enables the determination of the suspension power of a given formula based on low shear measurements and Bingham plots. We finally show the application of the suspension agent in a typical home care formula, focusing on the concentration of fragrance capsules and the suspension of visual beads in a liquid laundry chassis and the stability study of the formula as a function of time.

Materials

Solvay standard liquid laundry detergent composition

Table 1 shows the typical composition of the liquid laundry chassis used in this study. In order to study the dose response of Rheozan® BLC to the rheology properties of the chassis, its concentration was varied from 0 to 0.1% wt/wt as the activated cellulose fiber active, which is equivalent to 0 to 10% of Rheozan® BLC as is. Our Rheozan® BLC is supplied as a flowable and pumpable viscous liquid which will disperse easily in water and in liquid formulations. Hence, Rheozan® BLC can be added and dispersed at any step during the manufacturing of a liquid laundry chassis. In our study, Rheozan® BLC was added toward the end of the chassis formulation steps just before the final pH adjustment. Nevertheless, as Rheozan® BLC generates a yield as soon as it is dispersed in a liquid formulation, formulators need to be cautious with the formulation set-up and mixer selection to prevent air bubble formation during the formulation step.

Ingredients	Function	Composition as active (% wt/wt)
Rhodapex® ESB70 Sodium laureth (2EO) sulfate	Anionic surfactant	5.0
Rhodasurf® L7/90 Alcohol ethoxylate(Laureth-7)	Nonionic surfactant	10.0
Rhodacal® SSA Linear alkylbenzenesulfonate acid	Anionic surfactant	9.0
Coconut fatty acid Fatty acid	Soap	5.5
Repel-O-Tex® Crystal Nonionic polyester	Soil release polymer	1.0
Propylene glycol Solvent	Solvent	6.5
NaOH (40%)	Base	Qs pH
Citric acid (50%)	Acid	Qs pH
Rheozan® BLC Bacteria cellulose	Rheology modifier	0 – 0.1
Water	Solvent	Qs 100
pH		7.50

Tab. 1 Solvay Liquid Laundry Chassis Composition

Rheozan® BLC

Rheozan® BLC is a ready-to-use, flowable and pumpable activated cellulose fiber dispersion in water. It is manufactured in three steps: bacterial fermentation step, bacteria cellulose fiber purification step and activation step as shown in **Figure 1.**

Fermentation step

The cellulose fiber is obtained through the bacterial fermentation of starch by an acid resistant bacteria strain Komagataeibacter sp. The bacterial fermentation process is carefully controlled to produce high purity, high crystallinity, high modulus elastis and high aspect ratio bacteria cellulose fibers with a high yield. The yield rate regarding sugar to bacterial cellulose conversion is between 7% to 8%.

Purification step

After the fermentation process, the produced bacteria cellulose is subjected to a further purification process which includes isolation, precipitation and filtration to remove the bacteria and residues from the culture medium.

Activation step

In the final activation step, the obtained raw bacteria cellulose fiber is dispersed in water together with other ingredients such as an organic acid as preservative, a dispersant, etc. The mixture is then activated by subjecting it to high shear rate mixing to expand the very fine and high aspect ratio cellulosic fiber bundles. These expanded and entangled bundle structures form a cross-linked framework that facilitates swelling when in an aqueous solution, thereby providing excellent three-dimensional systems **(Figure 2)**.

Fig. 1 Rheozan® BLC manufacturing process

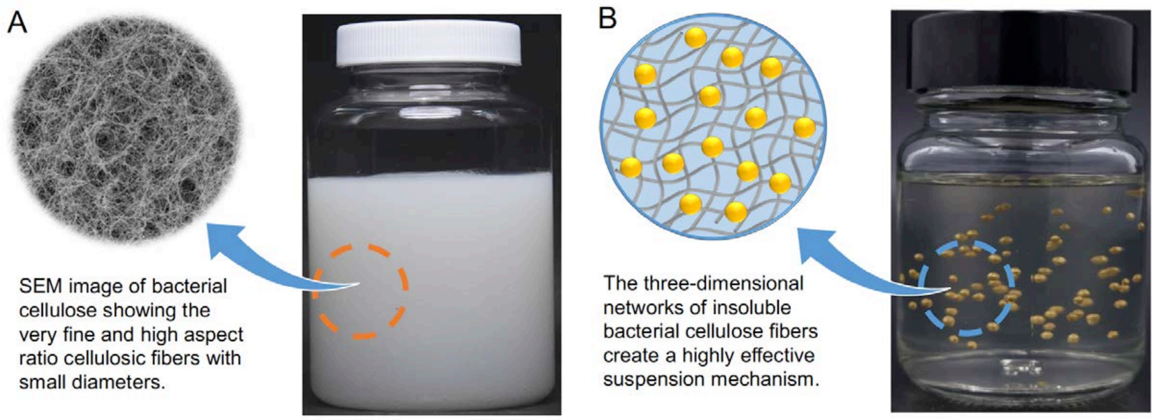

Fig. 2 1A: Rheozan® BLC, a ready-to-use natural liquid polymer. 1B: Rheozan® BLC in liquid aqueous formula, provides an excellent three-dimensional network with high suspension power.

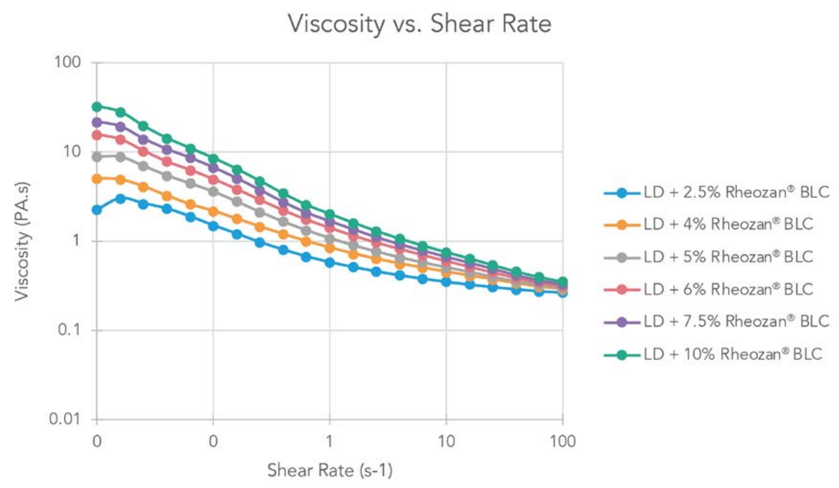

Fig. 3 Viscosity curve of Rheozan® BLC in Solvay liquid detergent (LD) chassis.

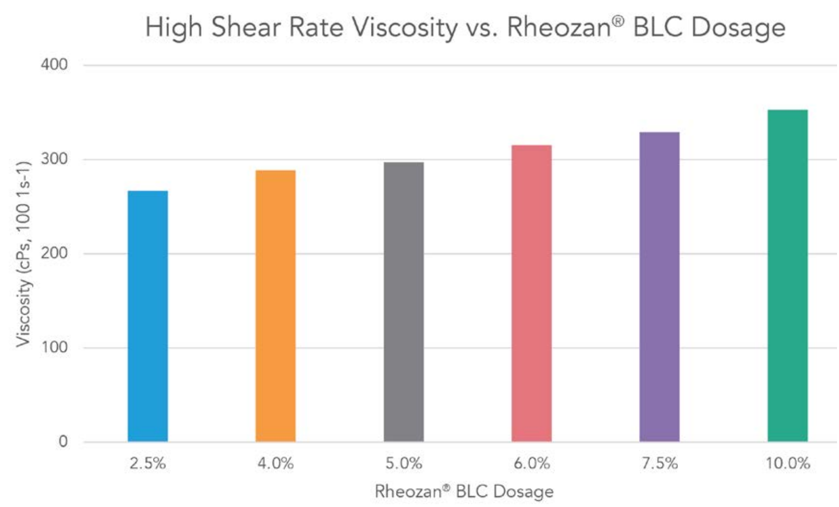

Fig. 4 High shear viscosity of Solvay liquid laundry (LD) chassis with Rheozan® BLC

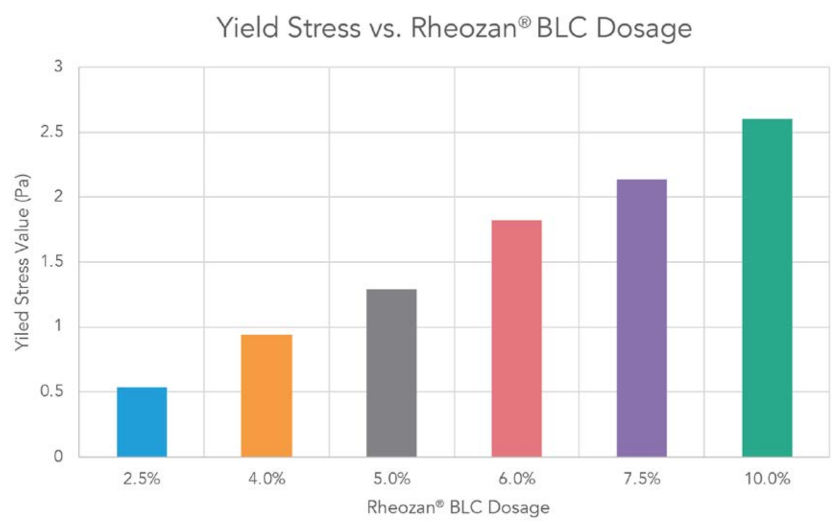

Fig. 5 Yield stress value of Solvay liquid laundry (LD) chassis with Rheozan® BLC calculated according to the Bingham equation using a shear rate range 2.5 to 25 s-1.

Methods

Equipment & principle of Lab measurements

The rheological property of Rheozan® BLC in a liquid laundry chassis, according to Table 1, was measured with Discovery HR-2 Hybrid rheometer from TA Instrument using concentric cylinder geometry of the following dimensions: cup radius: 15mm, rotor radius: 14mm and rotor height 42 µm. The measuring temperature was set at 25°C. Prior to measurement, the sample was pre-sheared at a shear rate of 100 s^{-1} for 120s and left for equilibrium for 60 minutes. A flow sweep measurement was done from shear rate of 0.01 to 100 s^{-1}. The yield stress value was calculated according to the Bingham equation using a shear rate range 2.5 to 25 s^{-1}.

Stability tests

To assess the suspending power of Rheozan® BLC, different particles such as fragrance capsules and pearlescent golden coated visual beads from Unispheres were suspended in the liquid laundry detergent chassis supplemented with Rheozan® BLC. To study the robustness and long-term storage stability of the Rheozan® BLC supplemented liquid detergent chassis, the formulations were stored at different storage temperatures such as 4°C, 22°C and 45°C for 3 months and their particle suspending power was compared to the liquid detergent without Rheozan® BLC. Furthermore, to study the long-term stability of Rheozan® BLC against enzymatic degradation, 2.5% Medley® Brilliant 300L from Novozyme was added to Rheozan® BLC supplemented liquid detergent chassis and the mixture was stored at 30°C and 45°C for three months and its particle suspending power was compared to the Rheozan® BLC supplemented liquid detergent without the addition of enzyme blends.

Results

Rheology of BLC in LLD

The flow behavior of the Rheozan® BLC supplemented liquid detergent chassis shows a shear thinning behavior with an increase of shear rates. The low shear rate viscosity of the sample increases exponentially with the concentration of Rheozan® BLC in the liquid detergent chassis **(Figure 3)**. However, the high shear rate viscosity (at 100 s^{-1}) changes only marginally i.e. less than 100 cPs when the Rheozan® BLC concentration increases from 2.5% to 10.0% **(Figure 4)**. The activated bacteria cellulose fibers form a continuous three-dimensional network in the liquid formulation to create yield stress to suspend particles, represented by the shear thinning rheology flow behaviors. As the bacteria cellulose active content in Rheozan® BLC is only ~1%, the active loading in the formulation is very low between 0.025% to 0.1% and for this reason, the high shear viscosities at 100 s^{-1} are not significantly impacted by the presence of the Rheozan® BLC network in the formulations.

Evaluation of yield stress

The yield stress value created by the Rheozan® BLC continuous three-dimensional network increases linearly with its concentration in the liquid laundry formulations as shown in **Figure 5**. Although the bacteria cellulose active loading in the formulation is very low, it can generate a remarkable yield stress value ranging from 0.5 to 2.6 Pascal, important for particle suspension performance while the viscosity at high shear rate, important for the final product flow, is not impacted. This yield stress value is sufficient to suspend particles ranging from fragrance capsules, opacifying particles and pearlescent visual beads in the formulation. Depending on the characteristics of the particles (such as size, density) to be suspended in a liquid formulation, formulators can estimate the required yield stress value, hence the required concentration of Rheozan® BLC in order to suspend the particles with long term stability.

Yield stress vs suspension power

The shear thinning flow behavior and the associated yield stress of the Rheozan® BLC supplemented liquid laundry chassis are the result of the continuous three-dimensional entanglement of the high aspect ratio bacteria cellulose fibers in the formulation. In other words, the chassis forms a gel i.e. a viscoelastic system that has both liquid and solid like properties. The solid-like property is associated with the three-dimensional network structure and the strength to hold the network together is represented by the yield stress value [1]. A solid particle in a liquid formulation will exert certain stress to the system, if the exerted stress is less than the formulation yield stress value, the network structure will deform elastically and suspend the particle stably in the liquid formulation. With this principle, typical fragrance capsules used in laundry detergents can be suspended with a yield stress value of less than 0.5 Pa. Hence 2.5% Rheozan® BLC is enough to supplement liquid laundry formulations to achieve long term suspension stability of the fragrance capsules. On the other hand, pearlescent golden coated visual beads with a particle size of 1.0 - 1.5 mm and density of 1.4 - 1.6 g/cm^3 will require yield stress higher than 1.0 Pa to suspend, hence it requires 5.0% Rheozan® BLC to stabilize the long-term suspension stability.

Typical application formula and its stability as a function of time

Rheozan® BLC shows not only excellent suspension power in liquid laundry formulation but also robustness and long-term stability at different storage temperatures. We suspended 0.3% by weight of fragrance capsules supplied by Eurofragrance and 0.3% by weight pearlescent golden coated visual beads supplied by Unisperses in Solvay liquid laundry chassis shown in **Table 1** with 2.5% and 5.0% Rheozan® BLC, respectively. The formulations show excellent storage stability with the fragrance capsules and the visual beads remain suspended even after more than 3 months storage at 4°C, 22°C and 45°C. Without the addition of Rheozan® BLC the fragrance capsules and visual beads would have been quickly sedimented from the liquid laundry chassis. Furthermore, when the Solvay liquid laundry supplemented with 5.0% Rheozan® BLC was added with Medley® Brilliant 300L (a blend of different enzymes, including cellulase) from Novazyme, at 2.5% by weight as supplied and subjected to a long-term storage stability study, its rheological properties as well as its suspension power remained unchanged after 3 months storage at 30°C and 45°C. These results imply that the bacteria cellulose fibers of Rheozan® BLC also have excellent stability against enzymatic degradation, especially by cellulase.

Throughout this paper we have elaborated the rheological properties, suspension power, storage as well as enzymatic stability and practical applications of Rheozan® BLC in a liquid laundry chassis. These interesting features of Rheozan BLC can also be applied to suspended particles in other home care formulations such as laundry sanitizer, hand dish liquid, hard surface cleaner, peroxide bleaching gel, etc.

Conclusion

The new suspension agent described in this paper presents several interesting features that make it perfectly aligned with current homecare market trends and needs. It is a natural and readily biodegradable product manufactured by fermentation of corn starch by specifically selected bacteria strains. It comes as pre-activated ready-to-use cellulose fibers in liquid form that can easily be integrated in liquid homecare detergent formulas, including when continuous processes are used at industrial scale. The additive brings unique suspension properties to homecare formula at low dosage, as evaluated by low shear rheology measurements correlated with the suspension power of the product in typical detergent liquids. This is exemplified in several formulations throughout this paper, such as a liquid laundry detergent with concentrated fragrance that demonstrates long term stability over several months at 45°C.
We believe this suspension agent is one of the first of a new generation of polymers arriving on the homecare market, with improved sustainability credentials from cradle to grave, i.e. natural sourcing and a good biodegradability profile. While the challenge of maintaining or improving the performance of synthetic non-biodegradable polymers with natural and biodegradable alternatives is a tough one, it has to be tackled in the next decade. Biotechnology based polymers, such as this suspension agent, are likely to be a key tool to reaching this ambitious goal.

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