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Thickening Agents for Surfactant Systems
Differentiation of Thickening Agents

The most common way to thicken a surfactant based formula is to use Sodium Chloride. In standard surfactant systems based on Sodium Laureth Sulfate (SLES) and Cocamidopropyl Betaine this works quite well. This thickening effect depends on the presence of an anionic surfactant (mostly SLES), and it works up to a concentration maximum. After this maximum the viscosity collapses, too much electrolytes lead to a destruction of the micelle network. Gelling agents like Xanthan Gum, Cellulose types or Carbomer types thicken or gel the water. In general they are electrolyte-sensitive and lead to an uncomfortable slimy appearance, which does not make them applicable as single thickener. In some cases they may be additionally required to achieve a yield point. Typical thickening agents for surfactant systems can be generally divided into 2 groups:

1. the hydrophobic, monomeric or oligomeric types with a low molecular weight. These types are mostly non-ionic surfactants, e.g. Glyceryl Laurate or Cocamide DEA.
2. the hydrophilic, polymeric types with a high molecular weight. These types are based on highly ethoxylated oleochemical derivatives, e.g. PEG-120 Methyl Glucose Dioleate.

The requirements for thickeners are continuously increasing. Very mild formulations, like baby shampoos, which contain generally a low amount of Sodium Laureth Sulfate, and furthermore often contain Sulfo succinates, are very difficult to thicken. Also PEG-free formulations, which are becoming more and more popular, are difficult to thicken. Special applications like dispenser packs require a special flow behaviour – which can be achieved by specific thickeners. Also in case of suspensions, e.g. of pearizers, capsules or Zinc Pyrithione, a special flow behaviour is advantageous.

Introduction

1. Flow behaviour
2. Temperature dependence of the viscosity
or PEG-200 Hydrogenated Glyceryl Palmate.

These two types of thickeners provide two important differences in performance: the flow behaviour and the temperature dependence of the viscosity.

1. Flow behaviour

The hydrophobic thickeners provide a shear thinning flow behaviour, that means the viscosity decreases with increasing shear rate. This can easily be observed by measuring the viscosity with a rotational viscometer at different speeds.

The hydrophilic thickeners provide a Newtonian flow behaviour, which means the viscosity is independent of the shear rate. It stays constant at different speeds of the viscometer.

Fig. 1 shows the difference in flow behaviour as a so-called flow curve, the viscosity plotted as a function of shear rate.

2. Temperature dependence of the viscosity

The hydrophobic thickeners provide a decrease of the viscosity at lower temperatures, but a mostly stable viscosity at higher temperatures.

The hydrophilic thickeners provide a strong temperature dependence of the viscosity: at lower temperatures the viscosity increases significantly, while at higher temperatures the viscosity decreases dramatically.

Fig. 2 shows the difference in temperature dependence.

Mechanism of Surfactant Thickening

To explain the different flow behaviour, it is necessary to understand the general mechanism of surfactant thickening (Fig. 3).

Basically, the thickening agents modify the micellar structure. In case of the polymeric hydrophilic thickeners, the hydrophobic groups of the molecules are incorporated into the surfactant micelles. This leads to bridging of the spherical micelles and/or an increase of the micelle size by the PEG-chains. The micelles have now a more limited space to move which leads in an increase of viscosity and a Newtonian flow behaviour.

The hydrophobic thickeners are also incorporated into the surfactant micelles, but since their hydrophilic head group is rather small, they change the shape of the micelles. The shape changes from spherical into rod-like. At rest, the micelles are arranged randomly, which leads to a high viscosity. With increasing shear rate, the micelles get oriented parallel – and hence the viscosity decreases. This process is reversible: with decreasing shear rate, the micelles are arranged randomly again – the viscosity increases.

Portfolio

Fig. 4 shows an overview of the thickener portfolio, divided into hydrophilic (marked with blue) and hydrophobic (marked with orange) thickeners. The differences concerning efficacy and other properties are discussed below.

Properties of Thickeners to be Considered

The main task of a thickener for surfactant formulations is of course to increase the viscosity. However, in order to have
a successful formulation, also the consumer perception is important. Here the flow characteristics and the application properties have to be considered. Good stabilizing effects can be obtained by choosing the right rheological profile and a low temperature dependence of the final viscosity.

In order to save costs, the efficiency of the thickeners is very important. Last but not least, also additional benefits like conditioning, moisturizing, refatting and solubilizing have to be considered when choosing a thickener system.

Consumer perception
For the consumer perception the type of formulation and/or the type of package is important. Shampoos or shower gels in their typical package require a different flow behaviour than a liquid soap in a dispenser pack.

Shampoos / Shower Gels
The results of an in house panel test showed that the consumer prefer a Newtonian flow behaviour for a shampoo / shower gel the.

A surfactant base has been thickened with different hydrophobic thickeners (ANTIL® HS 60, REWOMID® DC 212 S), the hydrophilic ANTIL® 120 Plus and a mixture of both types. The viscosity of all formulations was adjusted to be similar at elevated shear rate (50 rpm, Brookfield LVT).

The panelists were asked to evaluate the subjective perception of the flow behaviour and the subjective perception of the viscosity. They stirred with a spatula in the beakers and washed the hands with the formulas.

The results:
- The more shear thinning the flow behaviour, the worse was the consumer acceptance. The Newtonian flow is regarded as being more »rich«.
- The subjective ranking of viscosity by panelists corresponds best with Brookfield viscosity data measured at elevated shear speed: > 50 rpm, Brookfield LVT.

Fig. 5 shows the summary of the consumer tests and the technical data. It is obvious that the more Newtonian the flow behaviour was, the better was the subjective ranking. In the range of 60-75 rpm we found the same ranking as the panelists did.

Liquid soaps
In a separate consumer test the panelists were asked to judge the application property of liquid soaps out of a dispenser pack. Therefore, a surfactant system was thickened with a hydrophobic ANTIL® HS 60 and different hydrophilic thickeners like ANTIL® 171, ANTIL® 120 and ANTIL® 200 up to the same viscosity. The panelists were asked to make a ranking after application out of the dispenser packs.

Here, the shear thinning flow behaviour – provided by the ANTIL® HS 60 – was preferred, because the pumping was easier and there was no formation of strings. The viscosity decreases in the moment of pumping, and increases directly after pumping.

Stabilizing Effects
Dispersed particles, like pearlizers or Zinc Pyrithione, tend to separate in a surfactant formulation. Stoke’s rule describes the sedimentation speed, which is dependent of various parameters (Fig. 6). The only parameter which can be influenced with a thickener is the viscosity.

![Fig. 5 Consumer study on perception of shampoos and shower gels](image1)

![Fig. 6 Stabilizing effects](image2)
The higher the viscosity, the lower the sedimentation speed.

**Rheology**

The viscosity of a formula has to be as high as possible in order to reduce the sedimentation speed.

Best stabilization against sedimentation of dispersed particles is achieved by the hydrophobic thickener (shear thinning), because at low resp. no shear stress (storage conditions), the viscosity is high (Fig. 6).

**Temperature dependence of the viscosity**

A preferably low temperature dependence of the viscosity is important because of stabilizing effects, but also because of the consumer acceptance.

Fig. 2 shows that hydrophilic thickeners tend to show a strong decrease in viscosity at higher temperatures. On the one hand this leads to a higher sedimentation speed of dispersed particles. On the other hand, the consumer will not prefer to use a shampoo/shower gel with a very low viscosity.

At lower temperatures the hydrophilic thickeners tend to provide an increase of viscosity. This could lead to problems getting the product out of the bottle. Hydrophobic thickeners are weak at lower temperatures, here they tend to have a droop of viscosity.

Best shelf stability at high and low temperatures is obtained by using the Alkanolamides (REWOMID® DC 212 S or REWOMID® SPA), or a combination of both thickener types.

Fig. 7 shows the comparative data concerning the temperature dependence of the hydrophilic ANTIL® 120 Plus, the hydrophobic ANTIL® HS 60, a combination of both and the Alkanolamides REWOMID® DC 212 S and REWOMID® SPA.

The temperature dependence of the viscosity can be optimized by adjusting the ratio of both thickener types.

**Efficiency**

The efficiency of the thickening agents has been tested in different standard and PEG-free surfactant systems.

**Standard systems**

A. Sodium Laureth Sulfate (9% active) / Sodium Cocoamphoacetate (3% active, REWOTERIC® AMC)

B. Sodium Laureth Sulfate (9% active) / Cocamidopropyl Betaine (3% active, TEGO® Betain F 50)

C. Sodium Laureth Sulfate (5% active) / Disodium Laureth Sulfo succinate (2.5% active, REWOPOL® SB FA 30) / Cocamidopropyl Betaine (2.5% active, TEGO® Betain F 50), 1% NaCl

Fig. 8 shows the comparative data of the required amount of thickener in order to obtain a viscosity of 3500 mPas (Brookfield). The blue frames mark the hydrophilic thickeners; the orange frames mark the hydrophobic thickeners.

System A is the one which is the easiest to thicken. Here, ANTIL® 120 Plus and ANTIL® 200 are the most efficient hydrophilic thickeners, and REWOMID® SPA is the most efficient hydrophobic thickener.

System B required a higher amount of thickener. Also here ANTIL® 120 Plus and...
ANTIL® 200, followed by ANTIL® Soft SC are the most efficient ones.

System C requires the highest amount of thickener, due to the content of the Sulfsuccinate. This surfactant system can not be thickened with Sodium Chloride alone, so we added the maximum concentration before viscosity droop. Here REWOMID® SPA is the most efficient thickener.

Synergistic effects
By combining both thickener types, the total amount of thickener can be reduced, because the combinations show a synergistic effect.

In the example shown in Fig. 9, three hydrophobic thickeners have been combined with the hydrophilic ANTIL® 120 Plus. The single thickeners required a higher concentration than each combination of 1% hydrophobic thickener and the necessary concentration of ANTIL® 120.

PEG-free systems
PEG-free systems in general are difficult to thicken, and the choice of suitable PEG-free thickeners is limited. Fig. 10 shows the comparative efficacies of five PEG-free thickeners in order to adjust the viscosity of three PEG-free formulations to 3500 mPas (Brookfield). The pH-value was adjusted to 5 since this is the max. pH value allowed when using common preservatives like Sodium Benzoate.

A. 4.8% Sodium Cocoamphoacetate (REWOTERIC® AM C) / 4.9% CAPB (TEGO® Betain F 50) / 3.6% Disodium Lauryl Sulfsuccinate (REWOPOL® SB F 12 P)

B. 5.6% Cocamidopropyl Betaine (TEGO® Betain F 50) / 4.4% Lauryl Glucoside / 1.2% Coco Glucoside / 3.6% Disodium Lauryl Sulfsuccinate (REWOPOL® SB F 12 P)

C. 5.6% Sodium Cocoamphoacetate (REWOTERIC® AM C) / 4.4% Lauryl Glucoside / 1.2% Coco Glucoside / 3.6% Sodium/Disodium Cocoyl Glutamate

In all systems the natural based and Eco-cert conform ANTIL® Soft SC is most efficient.

PEG-free systems

In contrast to NaCl thickening agents provide added values

<table>
<thead>
<tr>
<th>Benefit/added value</th>
<th>NaCl</th>
<th>Evonik thickeners</th>
<th>Type of thickening agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hair conditioning</td>
<td>-</td>
<td>✓</td>
<td>VARISOFT® PATC</td>
</tr>
<tr>
<td>Moisturizing</td>
<td>-</td>
<td>✓</td>
<td>hydrophilic (PEG-Ester); ANTIL® Soft SC</td>
</tr>
<tr>
<td>Refatting</td>
<td>-</td>
<td>✓</td>
<td>hydrophobic (lipophilic)</td>
</tr>
<tr>
<td>Solubilizing</td>
<td>-</td>
<td>✓</td>
<td>PEG-Ester, ANTIL® Soft SC, TEGOSOFT® APM</td>
</tr>
<tr>
<td>Fast filling of final product (no / low stringiness)</td>
<td>✓</td>
<td>✓</td>
<td>hydrophobic</td>
</tr>
</tbody>
</table>

In all systems the natural based and Eco-cert conform ANTIL® Soft SC is most efficient.
Additional benefits
Thickening agents provide – additionally to the thickening property – a variety of added values. An overview of these benefits is listed in Fig. 11.

Hair conditioning
The quaternized amidoamine VARISOFT® PATC shows good compatibility with anionic surfactants and provides good conditioning properties out of a shampoo application. Especially when combined with Polyquaterium-10 and a silicone based conditioning agent like ABIL® T Quat 60 (Silicone Quaternium-22), it improves significantly conditioning properties like good combability and feel of the hair.

Moisturizing
Moisturizing effects are provided by the hydrophilic ethoxylated thickeners. Also ANTIL® Soft SC has a positive effect by a significant reduction of moisture loss after a rinse off treatment (Fig. 12). This has been proven by corneometer measurements conducted by an independent test institute. TEGOSOFT® PC 31 reduces the transepidermal water loss by 20%. This has also been proven by an independent test institute (Fig. 13).

Refatting properties
Hydrophobic thickeners, like TEGOSOFT® PC 31 and ANTIL® HS 60 provide refatting properties. This is proven by the measurement of the skin smoothness (FOITS), done by an independent test institute (Fig. 14).

Solubilizing
Solubilization can be achieved by the ethoxylated hydrophilic thickeners, and by ANTIL® Soft SC and TEGOSOFT® APM. This has been proven by solubilising Isopropyl Myristate in a surfactant system. ANTIL® Soft SC and TEGOSOFT® APM are more efficient in this example than standard solubilizing agents (Fig. 15).

Fast filling of the final product
Due to the shear thinning flow behaviour – provided by the hydrophobic types – the final product can be pumped into the final containers with a lower risk of forming «strings».
Benefits at a Glance

By choosing the right thickening agents one can achieve

- A good consumer acceptance of the final product.
- Good stabilizing effects.
- A reduction of the temperature dependence of the viscosity.
- A reduction of the total amount of thickener due to synergistic effects.
- Additional benefits like conditioning, moisturizing, refatting, and solubilizing.

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