

# Improving Foam Performance and Shelf Life Stability of One-Component Foams

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## **Abstract**

One-component foam (OCF) is widely used in construction applications, e.g. for mechanical fixation of door- and window-frames, as it perfectly combines gluing, gap sealing and insulating.

Besides physical foam properties and smooth foam application, the storage stability of one-component foam becomes more and more important since retailers and applicators request a shelf life stability up to 18 months and even more. Due to the fact that inside the cans a highly reactive prepolymer of isocyanate and polyol has to be stored for this prolonged period of time, shelf life issues are a growing field of concern for OCF manufacturers. Nevertheless, this is also a challenging field for additive suppliers. Degradation of the foam stabilizer or the cell opener can occur as well as skin formation inside the can. These effects can be influenced by the storage conditions, the raw material quality or other, unknown factors.

The demand for longer shelf life is increasing the requirements for additives to maintain well-balanced foam properties when a one-component foam is applied either directly after production of the can or after a certain storage time.

Therefore this paper discusses the mechanisms behind shelf life issues as well as the influence of foam additives on shelf life stability and strategies to mitigate these issues. We present novel additive concepts tailored for one-component foams allowing formulators to further improve cell structure, dimensional stability and shelf life.

## **Introduction**

In many aspects one-component polyurethane foam is different from standard two-component foam. Most obvious, of course, is the reverse sequence of reactions between the raw materials. In one-component foams at first the gel reaction occurs

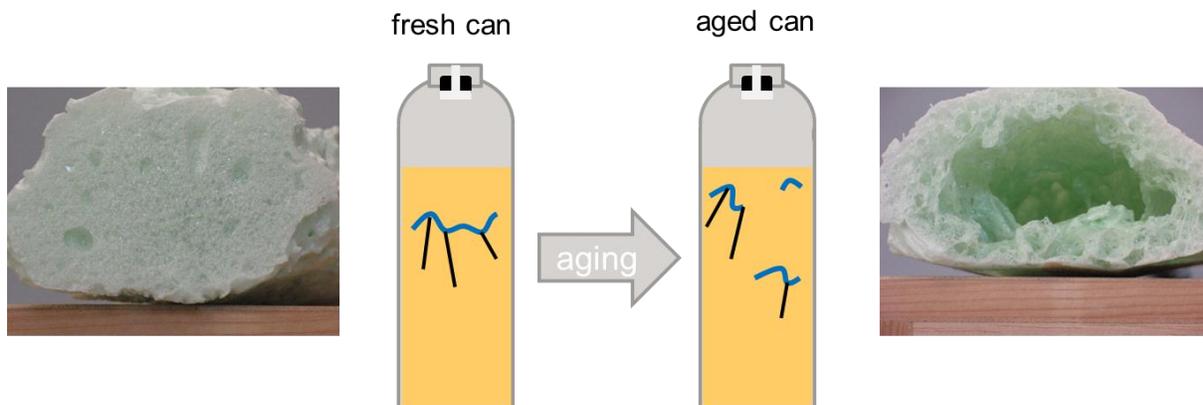
inside the can and afterwards the blow reaction happens with moisture from the surrounding, as soon as the foam is applied.

Inside the cans a prepolymer is formed by reaction between isocyanate (methylene diphenyl diisocyanate – MDI). MDI is used in great excess at an index of about 400-500. This prepolymer must be stored for a longer period of time inside the can together with a propellant (LPG - liquid petroleum gas), until the end-consumer applies the foam. These special characteristics of one-component foam are leading to certain challenges regarding the shelf life of such systems.

### Shelf Life Issues in One-Component Foam

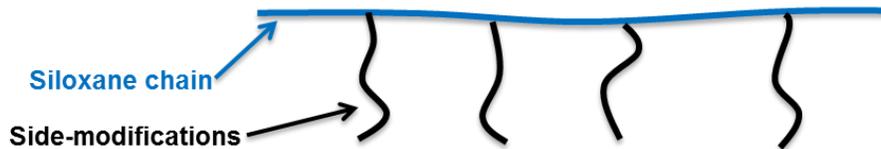
Several types of aging phenomena can occur inside an OCF can. One common phenomenon can be a viscosity increase which leads, in the worst case, to a complete solidification of the prepolymer. This is caused by an ongoing cross-linking reaction of the prepolymer due to impurities in the raw materials used, which catalyze the trimerization or allophanate reaction. As this is not a problem which is triggered or influenced by foam stabilizers, it is not discussed further in this paper.

Another issue is a cell coarsening or even a complete collapse of foam that is obtained from aged cans (Figure 1). In this case, a surfactant impact is obvious: The foam stabilizer has been degraded over time and this leads to a loss of stabilization activity. This chemical surfactant degradation is known to be caused by impurities of the raw materials that are used in OCF formulations. This includes free hydrochloric acid in the flame retardant and chlorinated paraffin or carbonic acids in ester polyols, castor oil or other NOPs.



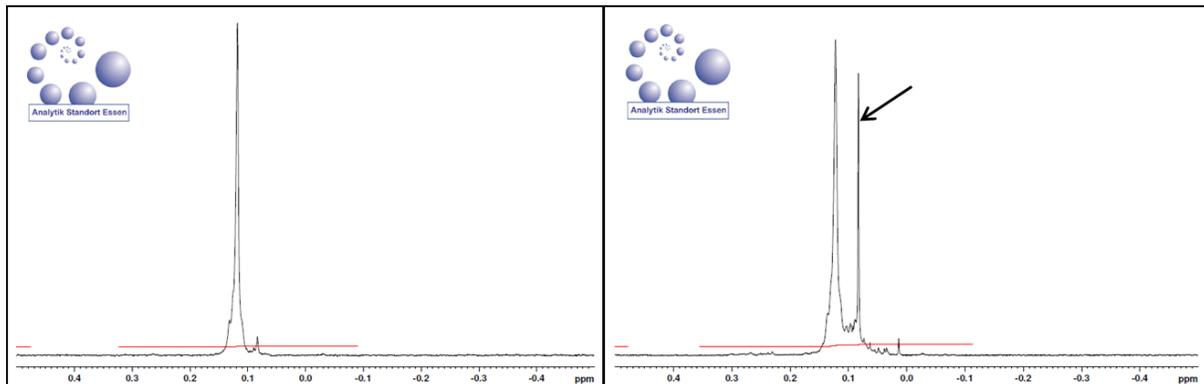
**Figure 1:** Cell coarsening effect/foam collapse due to chemical degradation of foam stabilizer in aged cans.

The degradation of the surfactant can be explained by cleavage of its siloxane backbone, which leads to a decrease in stabilizing performance or even to a formation of defoaming degradation products. The general structure of silicone foam stabilizers is shown in Figure 2.



**Figure 2:** General structure of silicone foam stabilizers.

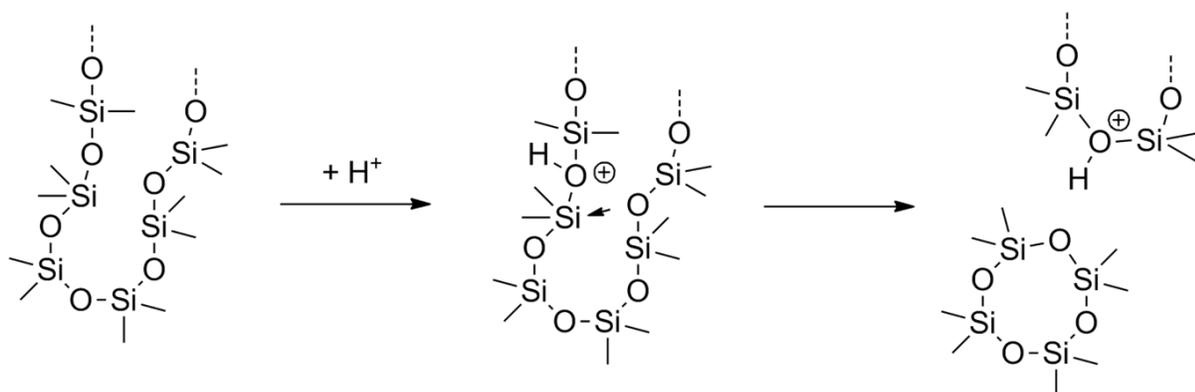
This cleavage of the surfactant's siloxane backbone itself can hardly be detected with available standards analytical methods inside aged cans due to the stabilizers low concentration and the complex composition of the prepolymer. However, specific degradation products, in particular octamethyl cyclotetrasiloxane ("D4"), can be seen with  $^1\text{H-NMR}$  spectroscopy. Figure 3 shows details of  $^1\text{H-NMR}$  spectra of mixtures of raw materials with a high acid value and a foam stabilizer. The left picture shows the spectrum of a freshly prepared mixture. There is no sign of degradation products visible.



**Figure 3:**  $^1\text{H-NMR}$  spectra of freshly prepared material (left) and of material that was stored 4 months at 40 °C.

The recorded spectrum on the right side of Figure 3 shows a clear degradation of the siloxane chain. A dedicated signal of quite high intensity (marked in the figure by an arrow) is visible which could be identified to derive from D4. The cleavage of Silicon-Oxygen-Silicon bonds within the siloxane chain is catalyzed by acids which can occur as

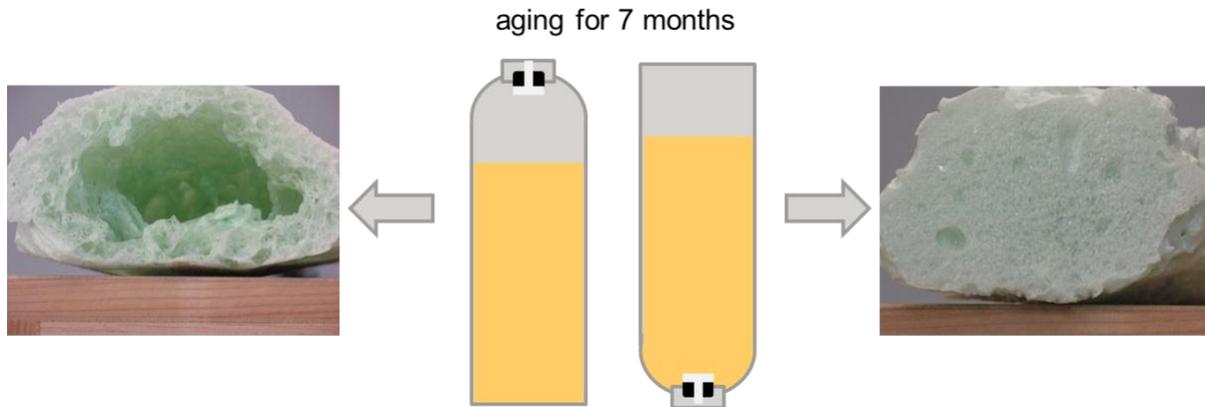
mentioned in several raw materials as an impurity. This leads to a breakdown of the siloxane backbone which in turn results in loss of stabilization potency. As suggested by the analysis shown, degradation products are lower molecular weight siloxanes, esp. cyclic compounds. The mechanism of this degradation process and formation of cyclic siloxanes is described schematically in Figure 4. It can be compared to a kind of re-equilibration process which is the inversion of siloxane chain formation during the established synthesis of siloxanes starting with D4 and related compounds.



**Figure 4:** Mechanism of siloxane chain cleavage by acids.

This degradation process is, of course, heavily influenced not only by the level of impurities level inside the raw materials, but also by amine type and -content, amount and structure of the stabilizer used, and other factors such as polyol type and storage conditions.

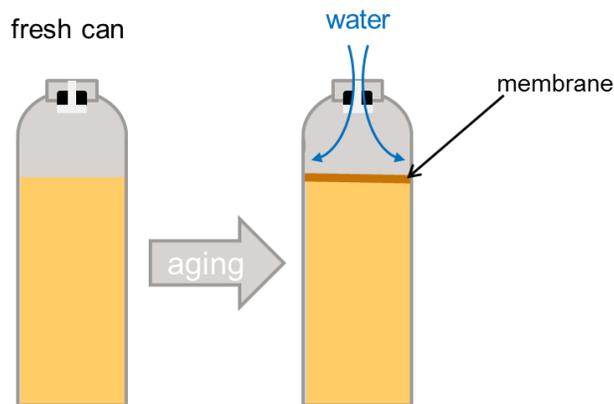
By conducting an unusual experiment, we found a hint towards another type of shelf life issue that leads in general to the same problem as the aforementioned one – coarse cells or foam collapse after a certain time of storage. Two cans, containing the same formulation with the same foam stabilizer were stored under identical conditions. But one can was stored upright, whereas the other one was kept up-side down (Figure 5).



**Figure 5:** Storage of two identical cans in two different positions.

The foam performance of each can was checked after seven months to evaluate, whether there is a difference detectable. As a result, the up-side down stored can was still showing good foam performance, but the other one, that had been stored upright, resulted in a collapse of the poured foam. Surfactant degradation seems unlikely in this case because this is a chemical process and would not depend on up-side down versus upright storage. So this issue must be caused by another mechanism.

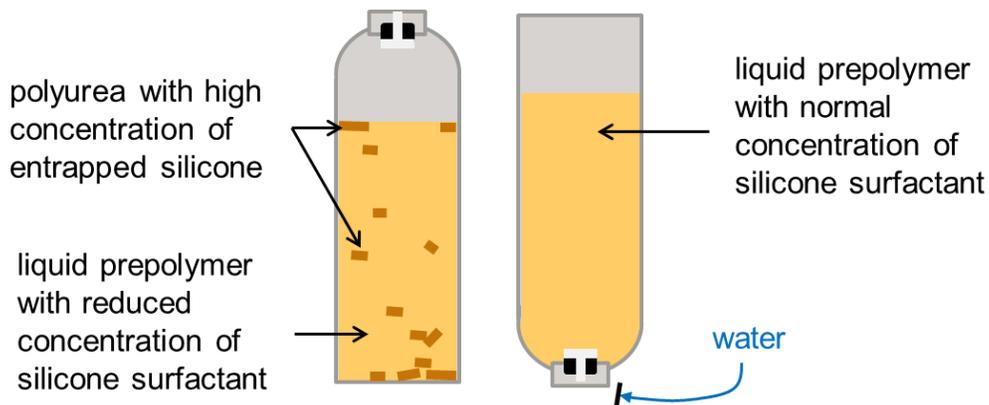
The observation in the last experiment leads to the last shelf life issue that is discussed in this paper, which is related to the formation of a membrane or a film on the prepolymer inside the can after storage for a longer period of time. This membrane mainly consists of polyurea and its formation is caused by moisture that diffuses through the valve into the can and reacts with excess isocyanate (Figure 6).



**Figure 6:** Formation of membrane inside a can.

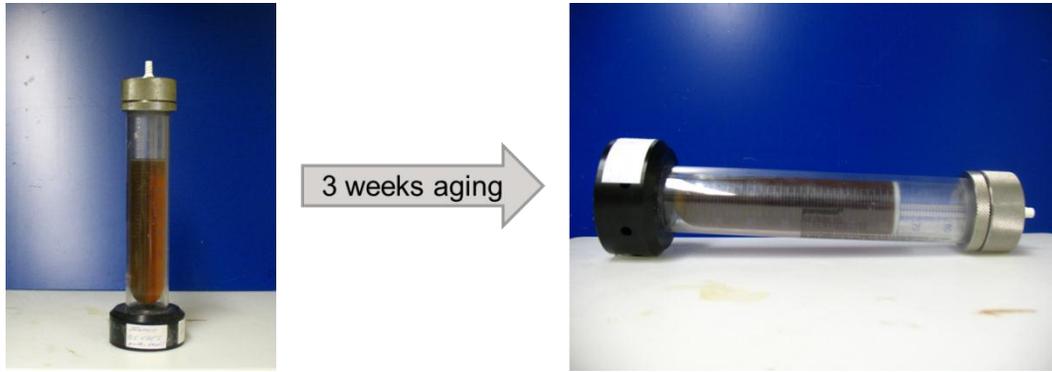
This water-isocyanate reaction leads to a cross-linking at the interface between the prepolymer and the gas phase and the resulting solid membrane can – in the worst case – prevent the can content from being applied.

In the experiment described in Figure 5 we did not observe a membrane formation. But in case of the upright stored can we found polyurea precipitations in the prepolymer. When the precipitate was analyzed, it was found that the surfactant was enriched in the precipitates and the level in the remaining liquid prepolymer was significantly reduced. In case of the up-side down stored can the prepolymer was still homogeneous with no precipitates of polyurea. As the valve is blocked by the prepolymer, water cannot enter the can because it immediately reacts with MDI in the valve. These mechanisms are shown in Figure 7.



**Figure 7:** Polyurea precipitates inside a can.

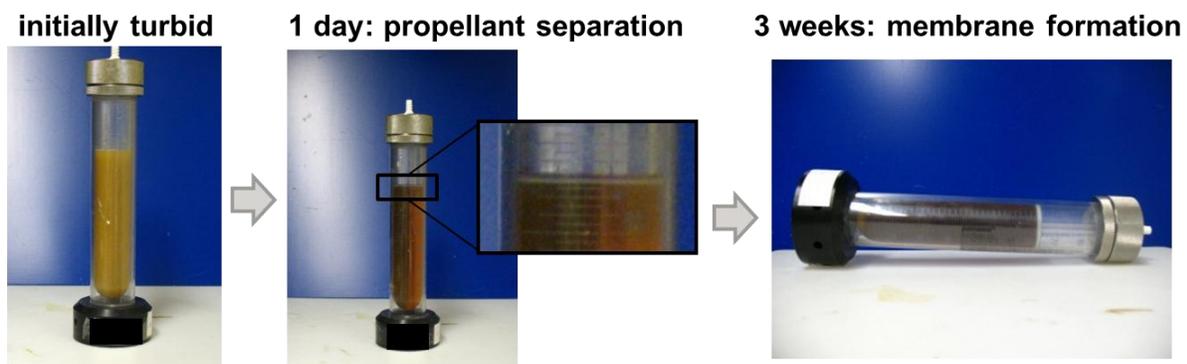
Obviously, there is a second mechanism of surfactant deactivation next to chemical degradation, which can be described as immobilization via inclusion into polyurea precipitates. This mechanism is, as mentioned, related to membrane formation. But even when no membrane is visible, small polyurea particles may be present which cannot be observed visually when releasing foam from the can. Of course, in real life storing the cans up-side down is not a solution to avoid shelf life issues because MDI diffuses into the rubber and blocks the valve. So there is need for another solution regarding this shelf life issue. As it is believed that different surfactants could show different susceptibility for this phenomenon, we examined several structures with high and with lower silicone content with regard to film formation. For this purpose we chose Parmasol glass tubes (see Figure 8) in order to see what is happening within the prepolymer when aging inside a can.



**Figure 8:** Experiments in Parmasol glass tubes.

The glass tubes are not only helpful by providing visual inspection of the content. The small amount of prepolymer per glass tube which results in a quite small surface area also helps to speed up the process of membrane formation.

To examine the correlation between stabilizer characteristics and membrane formation, several different surfactants have been tested by preparing completely formulated systems and storing them for a while at ambient conditions. The formulation itself was chosen to be quite prone to membrane formation. The foam stabilizers inside varied in their siliconophilic character: Some surfactants with higher silicone content and a selection of ones with lower silicone content were chosen and compared regarding their susceptibility to form a membrane inside the foam system. Figure 9 shows the result that was obtained using surfactants with higher silicone content.



**Figure 9:** Usage of stabilizers with high silicone content.

As it can be seen in the photograph, this kind of surfactants formed an initially turbid prepolymer blend with the chosen formulation. After a storage time of one day a

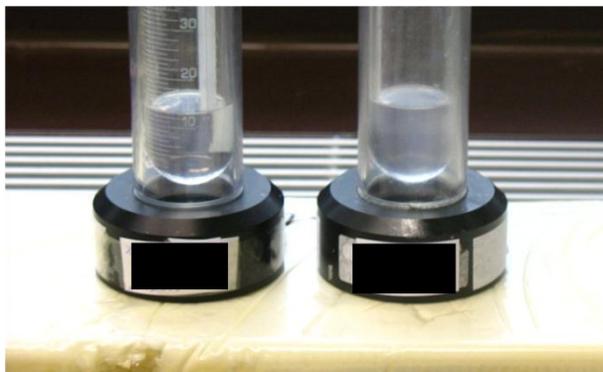
separation of propellant could be observed. After three weeks a solid membrane had formed on the liquid prepolymer.

For comparison, the same experiment was conducted with glass tubes containing a blend with stabilizers that feature lower silicone content. In these cases we obtained an initially clear prepolymer blend and observed no propellant separation subsequently. In particular, there was not observed a membrane formation during the period of storage.

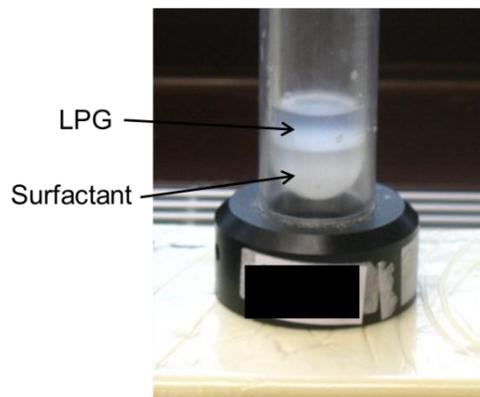
To further investigate the different behavior of the two stabilizer categories, silicone concentrations in the separating propellant phases as well as in the obtained membranes have been measured. For high silicone-content stabilizers we found enriched surfactant levels in the LPG phase as well as in the membranes. In some cases, the membranes consisted of about 25 wt-% of silicone surfactant, which is a strong indication that the stabilizer is enriched and integrated into the membrane. The separated LPG also contained free MDI besides the high amount of silicone. In experiments with blends containing moderate silicone-content stabilizers, we could not observe similar effects as there did not appear propellant separation and membrane formation to the same extent as with the highly siliconic stabilizers. But in case we were able to obtain a membrane after a long period of storage, the surfactant concentration was comparable to the level inside the prepolymer.

The enrichment of some stabilizers in the LPG phase suggests that there could be a difference in solubility of stabilizers with different structural properties in the propellant. To check this hypothesis, we examined the solubility of stabilizers with high silicone content and of stabilizers with moderate silicone content in LPG as a 1:1 mixture. Representative results are shown in Figure 10

**Stabilizers with high silicone content**



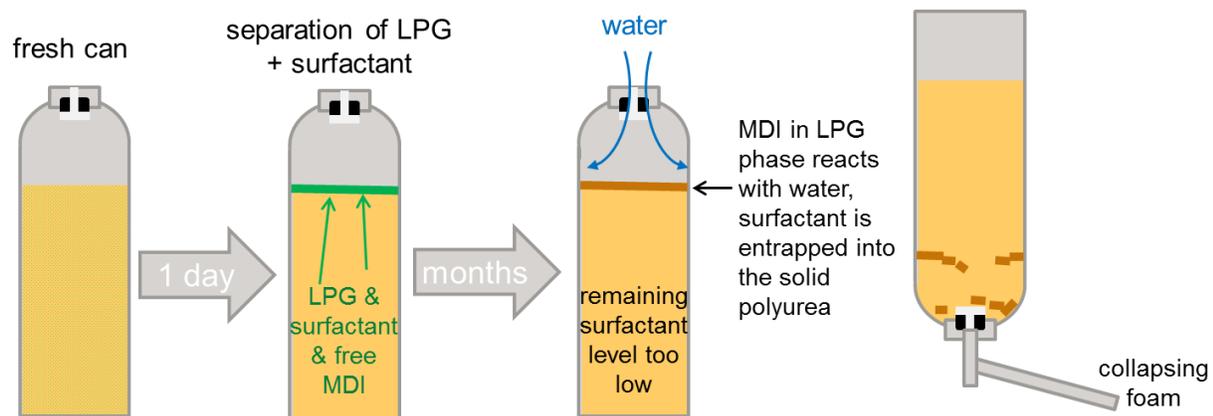
**Stabilizers with moderate silicone content**



**Figure 10:** Solubility of surfactants in LPG.

As a result it could be seen that surfactants with high silicone content typically are soluble in LPG, they form a clear or turbid, but single-phase solution (left side of the picture). Surfactants with moderate silicone content are poorly soluble in LPG. This can be seen on the right side of the picture, where the LPG has separated from the stabilizer.

We can conclude from the conducted experiments that formulations resulting into LPG separation are more susceptible to membrane formation than homogeneous prepolymer blends. This can be supported by the surfactant choice. Surfactants with high silicone content will support LPG separation and will migrate to the LPG phase due to high LPG solubility and poor prepolymer solubility. This means, highly siliconophilic products are more susceptible for this type of issues. The suggested mechanism is visualized in Figure 11: As a first step, LPG separates from the prepolymer blend and extracts surfactant and free MDI, which is hence enriched in the separated phase. As moisture diffuses through the valve into the can over time, a membrane or polyurea particles are formed by reaction of the water with free MDI. This results in a separated, solid material inside the can which contains a high concentration of surfactant. As a consequence the surfactant level in the prepolymer is lowered and could finally become too low for a proper stabilization. Even if there is no real membrane visible, this aging effect can occur on a microscopic scale.



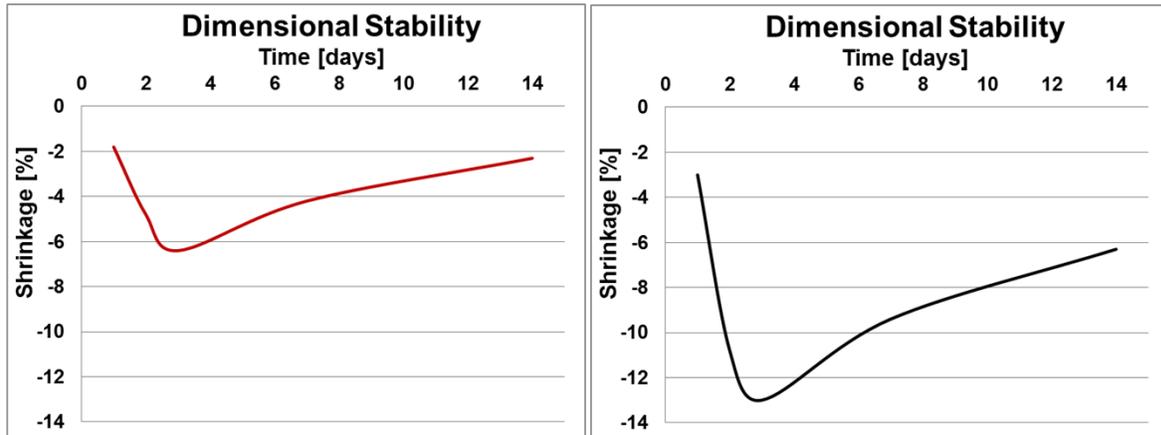
**Figure 11:** Mechanism of aging via surfactant inclusion.

As a helpful solution for this last-discussed aging mechanism it appears to use only stabilizers with moderate to low silicone content. But it must absolutely be considered, that this aging effect is not showing up in every system and that its appearance is limited to critical formulations only. Under non-critical conditions stabilizers with high silicone content offer clear performance advantages, e.g. good dimensional stability and high volume yield (see Figure 12). Consequently, the suitable stabilizer needs to be chosen

according to the actual system and its components (LPG composition, polyol type, susceptibility to separation, foam performance criteria...).

#### Stabilizers with high silicone content

#### Stabilizers with moderate silicone content

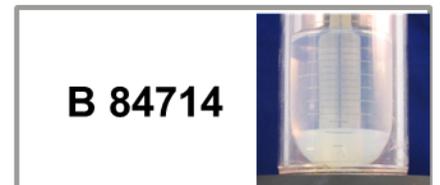
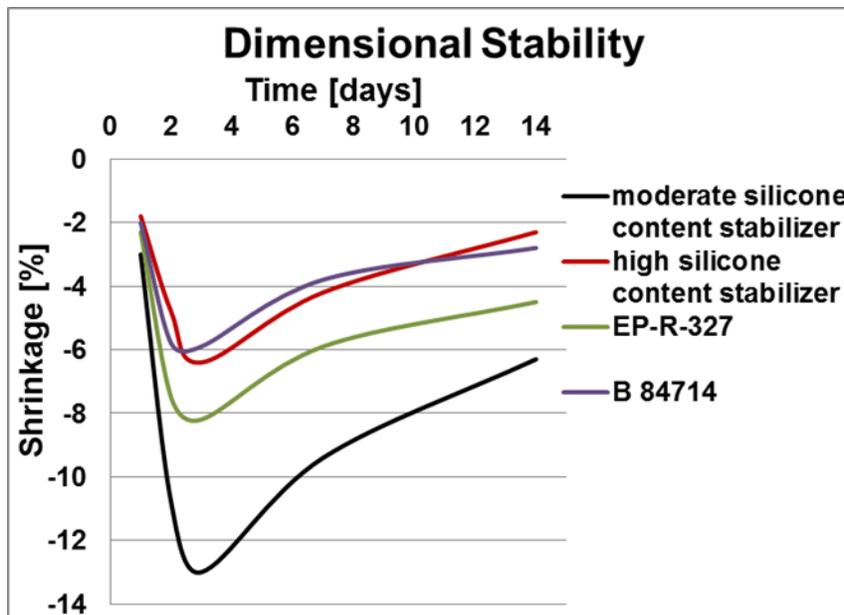


**Figure 12:** Comparison of dimensional stability of stabilizers with different silicone contents.

## Conclusions

To mitigate shelf life issues there exist multiple possibilities, corresponding to the different types of mechanisms behind the observed problem. Usage of better valves with lower penetration of moisture is one imaginable alternative. And, of course, impurities of raw materials need to be minimized to prevent the surfactant from chemical degradation. Another option is to use optimized foam stabilizers: As LPG separation is the starting point of some membrane formation issues and coarse cell/foam collapse phenomena, stabilizers should avoid separation to eliminate this type of shelf life issue.

Evonik's latest developments are targeting this objective: As shown in Figure 13, our newest generation of OCF surfactants offer state-of-the-art foam performance with low susceptibility to surfactant deactivation by separation effects.



**Figure 13:** Evonik's latest generation of OCF stabilizers show good foam performance (DMS in this case – left side), but are not prone to separation issues inside the can (low LPG solubility – right side).

The newly developed stabilizers, Tegostab B 84714 and EP-R-327 offer an excellent performance regarding dimensional stability (DMS) – as known from highly siliconophilic products – but show an outstanding shelf life in a broad range of formulations. We have optimized the LPG solubility behavior of these products for a very low susceptibility to shelf life issues examined and discussed in this paper, but we were able to keep the foam performance on a level of products with a very high silicone content.

## Biographies



**Dr. Jörg Diendorf** studied Chemistry at the University of Duisburg-Essen and received his Diploma in 2009. Afterwards he researched in the area of inorganic nanoparticles. He received his Ph.D. in Chemistry in 2012 with a thesis on synthesis and chemical-biological properties of silver nanoparticles. He joined Evonik's Business Line Comfort & Insulation in 2012. As Technical Manager he is now responsible for development of additives for rigid foam applications and technical customer service.



**Dr. Carsten Schiller** works in Evonik's Business Line Comfort & Insulation as Technical Manager Rigid Foam Development. His responsibilities include product development and technical customer service. After studying chemistry at the University of Hamburg, Carsten Schiller received his Ph.D. in Chemistry at the University of Bochum with a thesis on biomaterials for bone substitution in 2003. He changed to the University of Essen and continued his research activities in the department of Inorganic Chemistry. At the beginning of 2005 he joined Evonik.



**Sven Gahrens** works in the application technology team of Evonik's Business Line Comfort & Insulation and is responsible for technical service and product development for rigid foam applications. He started his career as a lab assistant 1993 at Th. Goldschmidt. In 1997 he left the company for different positions in the paint and coating industry. In 2009 he joined Evonik as a technician of chemistry in the polyurethane additives business.