

Release Agents for Low VOC HR-Molded Foam

Kai-Oliver Feldmann, Alfred Vuin, Annegret Terheiden
Evonik Industries AG, Goldschmidtstraße 100, 45127 Essen, Germany

kai-oliver.feldmann@evonik.com, alfred.vuin@evonik.com, annegret.terheiden@evonik.com

Abstract

Reducing the emission of volatile organic compounds (VOCs) is of global concern. For the manufacturing of molded foams the reduction of VOCs has two aspects. On the one hand, emissions of VOCs from foam parts need to be low to meet various limits set forth by the automotive industry. On the other hand, emissions of VOCs during manufacturing of molded foam, so called stack emissions, have to be below certain limits to conform to national legislation. While the first aspect has been a major driving force in the development efforts by all suppliers of foam raw materials, the second has had a large influence on release agent development. The influence of release agents on foam emissions has not yet been in focus. In this paper, we present a joint approach discussing both release agent related emissions, i. e. foam and stack emissions, for the first time. We present a detailed study of how release agents and application parameters influence foam emissions and how this influence can be minimized according to the VDA 278 and BMW chamber test. *Evonik Gorapur Hybrids* are introduced as today's most ideal product for meeting low foam and stack emission limits in high quality HR molded foam production. *Evonik Gorapur Hybrids* show a wide processing latitude with respect to foam emissions according to VDA 278 and significantly reduced foam emissions according to the BMW chamber test. *Evonik Gorapur Hybrids* also serve well for the reduction of stack emissions and are discussed in this context.

Introduction

Water-based release agents for HR-molded foam have been of interest for decades. Significant technical progress has been made in their formulation. Water-based polybutadiene emulsions are readily available and are used mainly for the manufacturing of NVH foams. Water-based wax dispersions for seating applications are also used, but very infrequently. This is due to the fact that in the large majority of applications, water-based release agents do not meet the standard set by state of the art solvent technology. For example, the quality of the foam surface may be lower, application may be more difficult and cleaning may be needed more often with water-based in comparison to solvent-based release agents. However, increasingly stringent environmental, health and safety regulations^[1] require the reduction of stack emissions and thus favor the use of water as solvent or co-solvent for release agents. With today's water-based technology, meeting both, regulatory and technical requirements seems mutually exclusive. Overcoming this hurdle, i.e. creating a pure water, stack emission free release agent with a performance matching today's solvent-based products will remain one of the major targets for release agent development in the next years.

In this paper we introduce Evonik Gorapur’s hybrid technology. Based on this technology, products are now available with a mixed water/solvent carrier with the same excellent performance as Evonik Gorapur’s solvent-based products. Compared to water-based products, a higher quality foam surface is obtained at a lower use level. Furthermore, build-up and cleaning requirements do not differ from those experienced using a solvent-based release agent. *Evonik Gorapur Hybrids* are today’s most sophisticated solution providing a perfect balance of state of the art technical performance and low stack emissions.

In the first section, *Evonik Gorapur Hybrids* are very briefly discussed in the context of stack emissions. The major focus in the second section of the paper is a general discussion of release agent related foam emissions including practical guidelines to achieve lower release agent related foam emissions.

Results and Discussion

1) Reducing Stack Emissions with *Evonik Gorapur Hybrids*

Replacing a solvent-based release agent with a water-based product can obviously be expected to result in lower stack emissions. Yet, the question remains how much the stack emissions are reduced by such an exchange. Experience shows that an absolute prediction is hampered by the multitude of parameters that influence stack emission. Thus, the emissions after replacement need to be measured under all circumstances. However, a reasonable estimation of the stack emissions before replacement is quite valuable. Such an estimate can be made when two preconditions are fulfilled. First, the current stack emissions (“*Stack Emissions*_{current RA}”) are known. These are greatly dependent on various process parameters^[2] and thus need to be measured for every facility individually. Second, carousel and venting system parameters are not varied during the exchange of release agents. This being the case, the stack emissions which are to be expected with the water-based release agent (“*Stack Emissions*_{new RA}”) can be estimated using the following, simple approximation. This equation holds for any release agent change and simply expresses the expected stack emissions as the product of the current stack emissions and certain release agent properties.

$$Stack\ Emissions_{new\ RA} \approx Stack\ Emissions_{current\ RA} \times \frac{Use\ Level_{new\ RA}}{Use\ Level_{current\ RA}} \times \frac{Solvent\ Content_{new\ RA}}{Solvent\ Content_{current\ RA}}$$

The factor “*Use Level*_{new RA} / *Use Level*_{current RA}” reflects the influence of different use levels of the new release agent to be implemented versus the one currently in use. This factor is greatly influenced for example by the complexity of the mold, the use of electrostatic spraying equipment or the characteristics of the foam formulation. Furthermore, it is of importance considering that today’s water-based release agents are most often employed at higher use levels than solvent-based release agents. It can usually be calculated after first small scale release agent trials at the existing production setup. The ratio “*Solvent Content*_{new RA} / *Solvent Content*_{current RA}” reflects the influence of the release agents’ solvent contents which is of major importance when comparing solvent-based with water-based release agent or

Evonik Hybrids. In this context it needs to be kept in mind that today's so-called water-based release agents usually contain between 15-30% of organic solvents. Actually, the wording "water-based" is slightly misleading in this context. Depending on the application, *Evonik Gorapur Hybrids* contain between 45 and 55% of solvent. The specific product which is used in the following foam study contains 55% of solvent. *Evonik Gorapur Hybrids* are designed to closely match the properties of solvent-based products. Thus, the use level of an *Evonik Gorapur Hybrid* is usually the same as for the solvent-based products ($Use\ Level_{new\ RA} / Use\ Level_{current\ RA} = 1$). Defining $Stack\ Emissions_{current\ RA} = 100\%$ and inserting the parameters above and an average solvent content of a state of the art solvent-type release agent (approx. 93%) stack emissions of 59%, i.e. a reduction by 41%, can be expected with this specific *Evonik Gorapur Hybrid*.

2) Reducing Release Agent Related Foam Emissions with *Evonik Gorapur Hybrids*

What are the key factors influencing the total amount of release agent related foam emissions? To what extent are the foam emissions related to the use level or the solvent content of the release agent? Does the drying time influence the overall emission? In order to answer these questions, a series of TDI foams was prepared with different release agents, varying drying times and spray amounts. The mold temperature was 63-65 °C. Selected foams were tested according to VDA 278.^[3] In order to make the test as critical as possible, it was ensured to test only very thin slices of the respective cushion's skin. This resulted in very high emission levels. These should not be taken as absolute values, but as a relative measure within this test series. The reported release agent related emission values are the sum of all release agent contributions of the VOC and FOG test. Finally, some foams were selected for testing according to a modified BMW chamber test method.^[4] Again critical testing was achieved by using foam samples with as much skin as possible. Details on sample preparation and the emission testing are given in the experimental section along with details on the foam formulation and foaming parameters. The employed release agents and their key characteristics are listed in table 1. All contain wax blends as active components and isoparaffines with a flash point^[5] of 56 °C.

Table 1. Types of release agents used in the study.

Release Agent	Abbreviation	Solvent Content	Water Content
Evonik Gorapur A3-type	R-A3	93%	0%
Evonik Gorapur Hybrid	R-Hybrid	55%	38%
Evonik Gorapur water-based	R-H₂O	5%	82%

Generally, three different categories of emissions can be identified in the analyses. The first category comprises any emissions originating from the release agents' solvents. These emissions contribute least to the overall emissions. They were clearly identified by comparison of the emission chromatogram of the test sample with that of a pure solvent sample run under the same GC/MS parameters (see experimental section for further details). In the following graphs, this category of emissions is labeled "solvent". The second category comprises all foam related emission. These were identified by testing a

foam sample which was prepared in a polyethylene foil without application of any release agent. The third category comprises all emissions which have neither been attributed to category 1 nor 2. These emissions originate from the active substances of the release agents and are labeled “active substances” in the following graphs.

The solvent and active substances emissions of foams prepared with **R-A3**, **R-Hybrid** and **R-H₂O** are depicted in Figure 1. All three release agents were sprayed at 12 g/m² (grams of release agent output per square meter mold surface) within three seconds and the resulting film was allowed to dry for 45 seconds. These settings can be regarded as realistic average spraying conditions. The solvent content of the employed release agents drops from 93% for **R-A3** to 55% for **R-Hybrid** to 5% for **R-H₂O**. However, in all cases emission of solvent from the foam are too low to be of any practical relevance (< 5 µg/g). Higher emissions result from the release agents’ active substances. However, these emissions do not correlate with the solvent/water contents of the release agents. Thus, *at average spraying conditions the water content of a release agent does not influence the release agent related foam emissions according to VDA 278*.

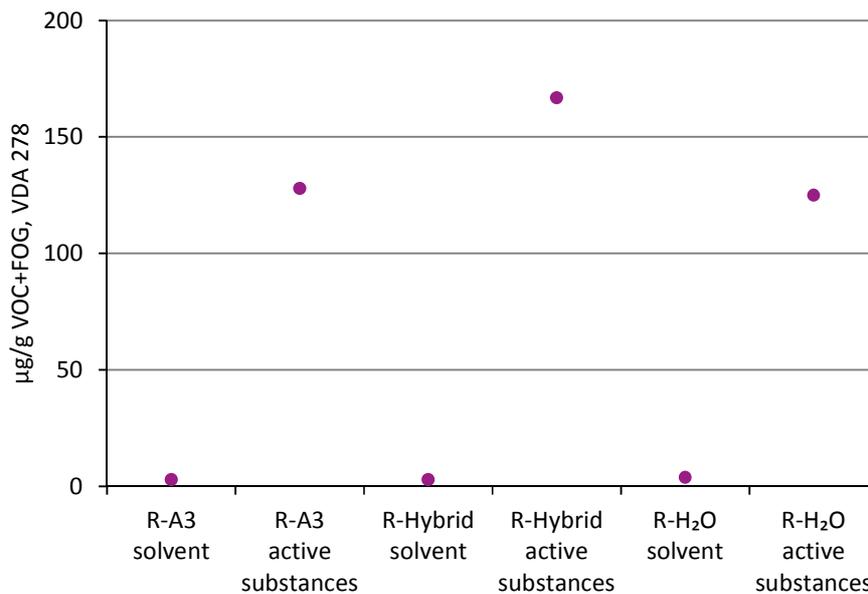


Figure 1. Overall foam emissions according to the VDA 278 VOC and FOG test resulting from solvent and active substances of release agents **R-A3**, **R-Hybrid** and **R-H₂O**; spraying conditions: 12 g/m², 45 sec drying time.

The solvent and active substances emissions detected for foams made with **R-A3** and **R-Hybrid** at spray amounts of 12 and 20 g/m², respectively, are displayed in Figure 2. When increasing the spray amount of **R-A3** from 12 to 20 g/m² the solvent emission increases from 3 to 42 µg/g while the active substances emission approximately doubles from 128 to 281 µg/g. In contrast, when **R-Hybrid** is sprayed at 20 g/m²

the solvent emissions are still $<5 \mu\text{g/g}$ and the active components emission level at 20 g/m^2 ($172 \mu\text{g/g}$) is essentially the same as at 12 g/m^2 ($167 \mu\text{g/g}$). Apparently, **R-Hybrid** is not as sensitive to extreme spraying conditions as a standard solvent-based release agent. **R-Hybrid** shows a wider processing latitude with respect to release agent related foam emissions. Overall, *Evonik Gorapur Hybrids lead to lower release agent related foam emissions in VDA 278 compared to a standard A3 product when a large amount of release agent needs to be applied.*

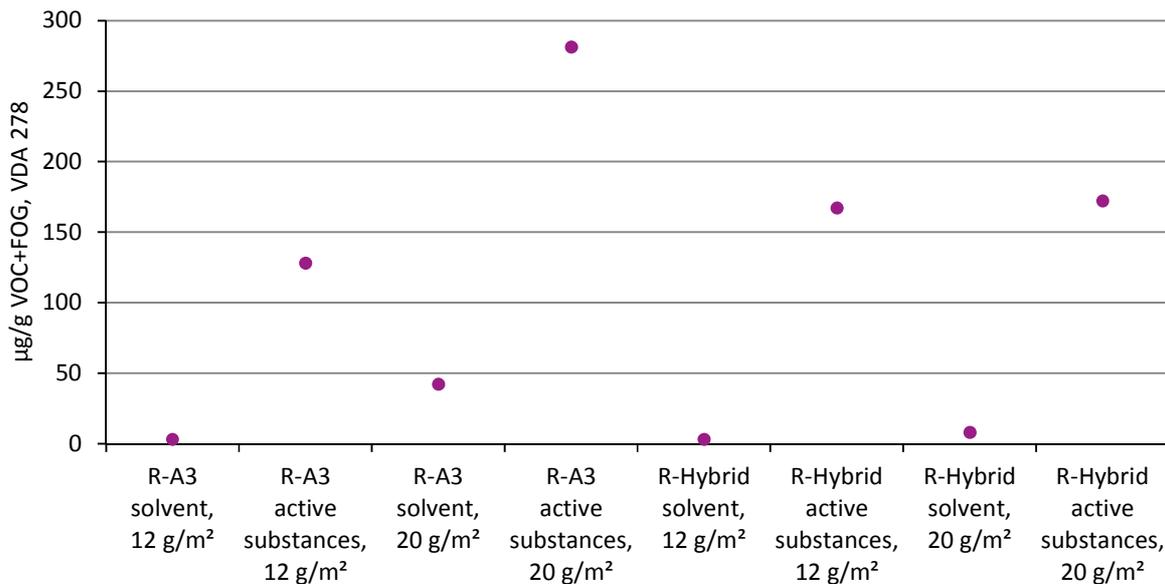


Figure 2. Overall foam emissions according to the VDA 278 VOC and FOG test resulting from solvent and active substances of release agents **R-A3** (12 g/m^2 and 20 g/m^2) and **R-Hybrid** (12 g/m^2 and 20 g/m^2); 45 s drying time.

The same conclusion can also be drawn from the visual inspection of the foam surface (Figure 3). With **R-A3**, spraying 20 g/m^2 at $65 \text{ }^\circ\text{C}$ mold temperature and 45 s drying time leads to the formation of solvent burns. Apparently, the maximum applicable amount for R-A3 is exceeded at 20 g/m^2 under the given conditions. In contrast, spraying 20 g/m^2 of **R-Hybrid** results in a foam with a good quality surface.

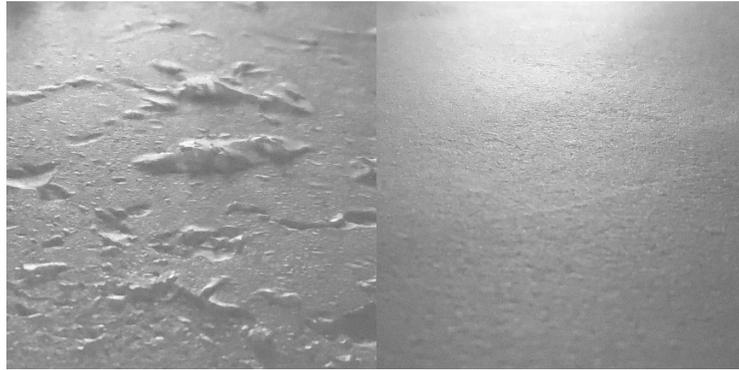


Figure 3. Close up photographs of the surface of foams prepared with **R-A3** (left) and **R-Hybrid** (right) at 20 g/m^2 , $65 \text{ }^\circ\text{C}$ mold temperature and 45 s drying time.

Emission values of active substances are depicted for foams prepared with **R-A3** using different drying times are given in Figure 4. From left to right the time allowed for the release agent to dry was 30 seconds, 45 seconds and 60 seconds. Apparently, increasing the drying time barely improves the emissions related to the release agent's active substances. Solvent emissions were $\leq 3 \text{ } \mu\text{g/g}$ in all cases. *At average spraying conditions an extension of the drying time does not significantly improve release agent related foam emissions according to VDA 278.*

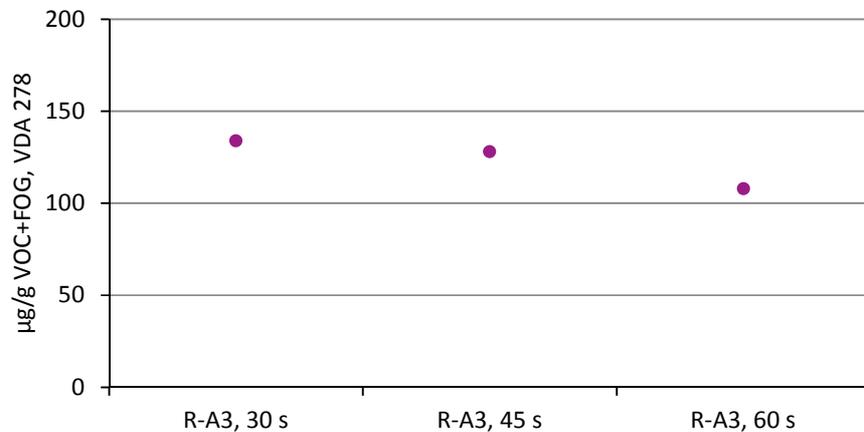


Figure 4. Overall foam emissions according to the VDA 278 VOC and FOG test resulting from active substances of release agent **R-A3** (12 g/m^2) at 30, 45 and 60 s drying time.

Selected samples of the VDA 278 testing series discussed above were also tested according to a modified BMW chamber test. It was found that the amounts of the various emitted substances according to the two different testing procedures are distinctly different. In the VDA 278 procedure, the emissions of the release agents' active substances form the largest share of the total release agent related emissions whereas the solvent contributes only a small share. In the BMW chamber test the opposite effect is

observed. The solvent related emission forms the most significant contribution to the total release agent related emissions. The solvent related emissions measured for foams made with low and high amounts of **R-A3** and **R-Hybrid**, respectively, are listed in Table 2. These values correlate with the total amount of solvent which was applied. Figure 5 shows a plot of the detected amount of solvent related emissions vs. the amount of solvent sprayed into the mold.

Table 2. Type of release agent, use level and solvent related emission according to a modified BMW chamber test.^[4]

Release agent	Use Level	Solvent Related Emission
R-A3	12 g/m ²	237 µg/m ³
R-A3	20 g/m ²	1638 µg/m ³
R-Hybrid	12 g/m ²	46 µg/m ³
R-Hybrid	20 g/m ²	290 µg/m ³

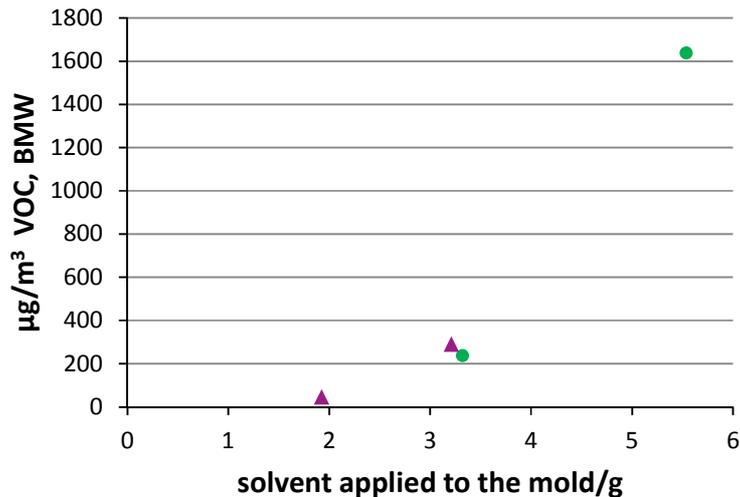


Figure 5. Solvent related foam emissions according to a modified BMW chamber test vs. the amount of solvent sprayed into the mold; ▲ R-Hybrid, ● R-A3.

Apparently, the BMW chamber test is significantly more critical with respect to the detection of solvent related emission. If the spray amount is high, a high solvent related emission is to be expected. In some cases it may not be an option to decrease the spray amount, for example if a very complex mold is used or the foam formulation is exceptionally challenging. In this case, switching from a standard solvent-based release agent to an *Evonik Gorapur Hybrid* significantly improves the overall emissions.

Experimental Details

1) Foam formulation and foaming procedure

The foam formulation used in this study is given in Table 3. The relatively high SAN-polyol content results in a comparatively hard foam which allowed more precise cutting of foam samples for emission testing.

The foams were prepared via hand foaming. Polyols, amines, water and surfactant were weighed into a disposable polyethylene beaker and premixed with a blade agitator at 1000 rpm for 60 s. Isocyanate was added and the resulting mixture was stirred at 2500 rpm for 7 seconds. The foaming mixture was then filled into the mold of 10 cm height with a right angled isosceles triangle base with equal sides of 40 cm. The mold temperature was 62-65 °C and demolding time was 5 minutes. Immediately after demolding, the foam was opened by crushing and it was then stored at 21 °C for 24 h before samples were taken.

Table 3. Foam formulation.

Component	details on foam components	pphp
Polyetherpolyol for HR foam	OH-Number = 31 mg KOH/g	40.00
SAN-Copolymer Polyol for HR	SAN content 43%, OH-Number = 20 mg KOH/g	60.00
Tegoamin® DEOA 85	Diethanolamine (85% in water)	1.00
TEGOAMIN® 33	33% Triethylenediamine, 67% Dipropyleneglycol	0.41
TEGOAMIN® BDE	70% Bis(2-dimethylaminoethyl)ether, 30% Dipropyleneglycol	0.06
TEGOSTAB® B 8738 LF 2	Low to medium activity TDI surfactant.	0.70
Water		3.83
Toluene diisocyanate (T80)	80% toluene-2,4-diisocyanate, 20% toluene-2,6-diisocyanate	40.39

2) Mold preparation and spraying procedure

The release agent was manually sprayed using atomization air pressure of 1.5 bar and a release agent output of 71 g/min. For an application of 12 g/m² and 20 g/m², the release agent was applied for 3 s and 5 s respectively. Drying time was 45 s unless indicated otherwise. Foam samples were taken from the third foam prepared with the release agent of interest. I. e. when changing release agent two foams were prepared and disposed of before a sample of the third foam was taken. By this means contamination from the previously applied release agent were minimized. Blank values were obtained from foams prepared by lining the mold with polyethylene film.

3) Sampling

Samples were cut from the foam cushions of interest according to Figure 6. Using a cleaned, not lubricated band saw blade, the foam was cut along the dashed lines 1-4 resulting in one larger block (12 x 12 x 10 cm; grey) which was used for testing according to the modified BMW chamber method, and one smaller block (2 x 2 x 10 cm, grey) from which 2 mm was cut from the A side.. A sample was taken from the resulting foam (2 x 2 x 0.2 cm) for testing according to VDA 278. All foam samples were wrapped in aluminum foil and sealed in a polyethylene bag.

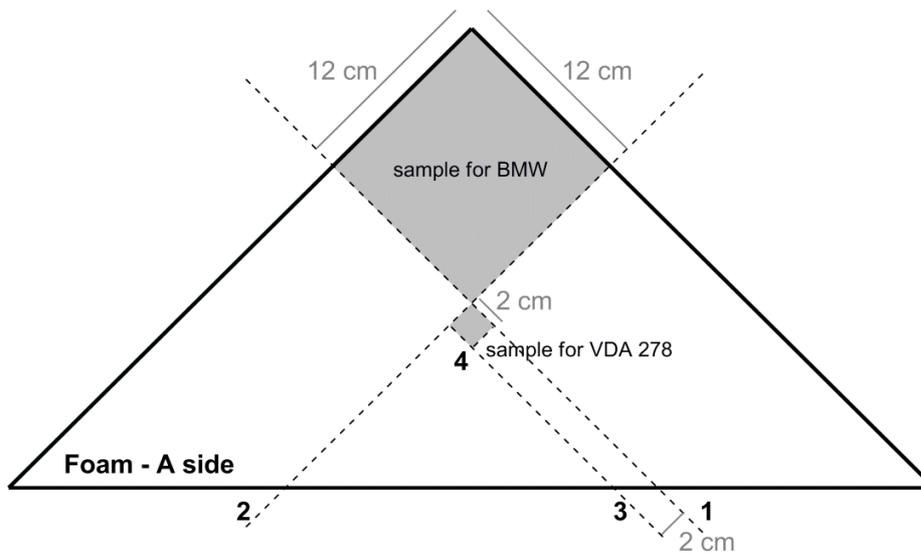


Figure 6. Cutting of foam samples.

4) VOC/FOG Analysis according to VDA 278^[3]

Full details of the method can be found in the test method PB VWT 709/ VDA 278^[3]. Briefly outlined, the method works as follows. An exactly weighed sample of approx. 15 mg of the skin of a molded foam is cut into three pieces which are placed in a sample tube. The tube is heated to 90 °C for 30 min while 65 mL/min of cleaned air is passed through the tube. Under these conditions volatile organic compounds (VOCs) are thermally desorbed off the foam sample and carried away in the air flow. The air flow from the sample tube is then passed through a cryo trap at -150 °C. This causes the VOCs to freeze and remain in the trap. Essentially the entire VOC emissions of 30 minutes thermal desorption are thus collected. Subsequently, the collected VOCs are evaporated by heating the cryo trap to 280 °C (10 °C/s ramp) and the gaseous VOCs are analyzed using a GC/MS (Agilent 7890 with a Agilent 19091B-115, Ultra 2, 50 m * 0,32 mm dF 0,5µm collumn and a Agilent MSD 5975 detector). Calibration of the GC before the analysis using toluene as the standard allows the quantities of the detected substances to be reported as toluene equivalents in µg per gram of foam. In order to analyze the FOG emissions the procedure is repeated but

this time the sample tube and the foam within is heated to 120 °C instead of 90 °C and calibration is done using hexadecane.

5) Foam emission quantification according to a modified BMW chamber test^[4]

In the original version detailed in BMW test method GS 97014-3^[4] this analysis is a chamber test method in which an entire foam part is tested within a 1 m³ test chamber. While all parameters from the original method are followed, the chamber in the modified version used in this paper is downsized to 30 l. It has been demonstrated that the emission values obtained with the modified method correlate very well with results from the original test. Briefly summarized, the modified test is carried out as follows. The test is a three part procedure. First the foam sample is conditioned in order to assure reproducible results. Then, the sample is placed in the test chamber and all substances emitted from the foam are collected. In the last part, the collected emitted substances are analyzed. For foam conditioning, an exactly weighed 30 g sample of foam is placed in a 30 L glass chamber which is flushed with 15 L of cleaned synthetic air (<0,1 ppm total content of hydrocarbons) at 23 °C and 50% relative humidity for seven days. The foam is removed from the glass chamber and is immediately placed into the test chamber which has been cleaned and tested to be free of any contamination of previously tested foams and subsequently been preheated to 65 °C. The loaded test chamber is flushed with 200 mL/min of cleaned synthetic air at 5% relative humidity and 65 °C for 1 hour. The entire airflow that is exiting the chamber is passed through a Tenax[®] tube (Tenax[®] TA, porous polymer resin based on 2,6-diphenylenoxid, Scientific Instrument Services, 1027 Old York Rd., Ringoes, NJ 08551). All substances emitted from the foam are adsorbed on Tenax[®]. The Tenax[®] tube is then transferred into the GC/MS setup as described above for the VDA 278 setup. The substances adsorbed on Tenax TA[®] desorbed 280 °C and transferred into the setups cryo trap at which point the analysis and quantification of the emitted substances proceeds exactly as described above.

Summary

In summary, the study revealed that there are two different types of release agent related emissions, i. e. those originating from the release agents' active components and those originating from the solvent. The total of release agent related foam emissions are dominated by the former in the VDA 278 test and by the latter in the BMW chamber test. In the VDA 278 test series it was found that at average spraying conditions neither the water content of a release agent nor an extended drying time significantly influence the release agent related foam emissions. However, if release is difficult, for example due to complex molds or challenging formulations and an increased amount of release agent is therefore necessary, *Evonik Gorapur Hybrids* are ideal for reducing foam emissions. In this case *Evonik Gorapur Hybrids* are superior to solvent-based release agents. This is especially of interest, as *Evonik Gorapur Hybrids*' overall performance is equal to that of solvent-based release agents. Despite water contents between 30 and 50% they provide the same excellent surface quality and release performance for which *Evonik Gorapur*'s state of the art A3 isoparaffine-based release agents are known. In the BMW chamber test series it was found that the amount of solvent which is sprayed into the mold correlates with the

release agent related foam emissions – the less sprayed the lower the emissions.. Thus, *Evonik Gorapur Hybrids* do not only provide an excellent tool for the reduction of stack emissions, but also for reducing release agent related foam emissions according to the BMW chamber test.

References

- [1] for example German legislation; „31. Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes (Verordnung zur Begrenzung der Emission flüchtiger organischer Verbindungen bei der Verwendung organischer Lösemittel in bestimmten Anlagen)“, 31. BImSchV, **2013**.
- [2] “Foam Additives and Release Agents for the Production of Low VOC Molded Foams Fulfilling VDA 278 Requirements and Reducing Stack Emissions”, E. Emmrich-Smoczyck, A. Terheiden, M. Vidakovic, *PU Magazine* **2014**, 11, 2, 103.
- [3] “Thermal Desorption Analysis of Organic Emissions for the Characterization of Non-Metallic Materials for Automobiles”, VDA 278, October **2011**.
- [4] “Emissions measurement with air exchange in a testing chamber”, BMW Group Standard GS 97014-3, April **2011**.
- [5] measured according to DIN EN ISO 2719

Biographies

Dr. Kai-Oliver Feldmann received his Ph.D. in Chemistry from the University of Münster, Germany, in 2012. He joined the central development and application technology of Evonik Industries AG's polyurethane additive business in 2013. His major projects concern development tasks for the Evonik Gorapur release agents as well as Tegostab surfactant and Ortegel performance additives product ranges for molded foam.



Alfred Vuin joined Evonik GORAPUR GmbH as a technical manager in 2011. His projects concern release agent development and technical support for automotive applications.



Dr. Annegret Terheiden received her Ph.D. in Chemistry with an emphasis on interfacial and physical chemistry at the University of Duisburg-Essen, Germany. In 2006 she joined the former Goldschmidt GmbH as a technical manager for flexible foam where she was responsible for the development of additives for flexible foam applications. Today she is working at Evonik Industries AG as global technical director for molded foam applications.

