Chemical blowing agents in the rubber industry. Past – present – and future?

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SUMMARY
Whether it be foamed aluminium in the A-pillar of a passenger car, Ytong autoclaved aerated concrete, Elastolit PU rigid foam or Semperform EPDM window profile – whatever the class of materials, there will inevitably be foamed versions. Some of these are new while others have been established for decades, and they are used in a wide range of industrial and consumer-oriented applications. Defined foam structures have therefore become an essential tool in modern materials development. This article outlines the technical aspects of chemical blowing agents and the special mechanisms by which they act, which lead to the targeted production of different elastomeric foams. In addition, it reports on the status of the current REACH discussion concerning the blowing agent azodicarbonamide.

INTRODUCTION
The most obvious reason for using foams or foamed materials lies in the lower density, and therefore the weight reduction, of a component when a gas and a solid form a two-phase system. However, the presence of the gas and the large number of interfaces within the foam structure mean that other properties of the foam are also modified significantly by comparison with the solid material. The number, size, structure and distribution of the cells determine the foam’s conductivity for sound, heat and electromagnetic fields, its elasticity, compressibility, buoyancy, resilience and surface hardness.

There are two traditional methods available for producing foams in the plastics industry: physical foaming and chemical foaming. In the physical foaming process, a solvent or inert gas is injected as a supercritical fluid into thermoplastic melts, where it dissolves under high pressures. In the subsequent shaping step (extrusion or injection moulding), it evaporates with reducing pressure and expands the melt. The factor that regulates the even formation and fixing of the foam structures is the defined cooling, i.e. the increase in extrudate viscosity. Particularly low weights per unit volume can be achieved with physical blowing agents, since they are able to introduce large amounts of gas into the thermoplastic melt. However, this requires considerable investment in special equipment and high-precision process control. Numerous scientific studies have been carried out into the physical foaming of elastomers [1], but up to now its commercial importance is limited because of problems with the stability and homogeneity of the foam structures and with process reproducibility [2]. Another physical process is mechanical foaming, which is restricted to the liquid form of elastomers as latex emulsions. Here, the art of foaming lies in the design and engineering of suitable mixing equipment [3].

The state of the art for solid rubbers is foaming with chemical blowing agents. These are solid inorganic or organic compounds, which are added to the rubber compounds during the mixing process. The particles break down under the action of heat, releasing gaseous products. If the blowing agents are distributed evenly, chemical foaming leads to uniform cell structures and surfaces. Foamed products can be produced without any major outlay on equipment, on standard machinery that is also used to produce non-foamed products. This provides the producer with a high degree of adaptability and flexibility in terms of manufacturing technology.
CHEMICAL BLOWING AGENTS AND THEIR REACTIONS

The inorganic blowing agents include ammonium, sodium and potassium carbonates and hydrogen carbonates (bicarbonates) which, under their trivial names “hartshorn salt”, “bicarbonate of potash” and “bicarbonate of soda”, have been used for leavening baked goods at least since the days of German chemist Justus von Liebig in the 19th century. Consequently, bicarbonates – as well as nitrate compounds – were the first chemical blowing agents for plastics. These compounds give off CO₂ and water under the action of heat and acids. Among the many possible acids, hydrogen phosphates, tartaric acid and citric acid are particularly suitable, with the last of these giving off CO₂ on its own when heated (Figure 1). It is important to emphasise the physiologically harmless nature of the blowing agents and their decomposition products.

All the above inorganic blowing agents decompose endothermically, i.e. heat has to be supplied continuously to maintain the blowing reaction. This means that, on reaching the decomposition temperature, the blowing agent decomposes gradually rather than suddenly. The rate of gas release corresponds to the supply of heat. Without heat input, the reaction rapidly comes to a standstill. In practice, the consequence of this characteristic is that hydrogen carbonates and vulcanising chemicals have to compete for thermal energy. Slow, even release of gas, the good diffusivity of CO₂ in rubbers and the “thermal slowing” of the curing reaction lead to open, unevenly coarse cell structures and occasionally to the risk of irregular surfaces. The combination of bicarbonate and acid activator gives finer cell structures while maintaining the basic characteristics.

The group of organic blowing agents consists of various compounds that release mainly nitrogen. Common to all of them is their exothermic mode of reaction, i.e. when the decomposition temperature is reached, the breakdown of the blowing agent releases heat which in turn activates adjacent particles of blowing agent to react. Heat of reaction delivers additional activation energy right where it is needed, and so the entire stock of blowing agent reacts promptly and unstoppably in a cascade-like process.

One of the most widely established of the exothermic blowing agents, and the most important in terms of volume, is azodicarbonamide (azo or ADCA), a yellow-orange powder that was synthesised for the first time in 1892 [4] and was first used for foaming PVC in the 1930s. In a complex cascade reaction, pure azo decomposes at approx. 200°C liberating N₂, CO and, in the presence of water, NH₃ (Figure 2). Solid residues that remain are urazole, hydrazodicarbonamide (biurea) and, in the absence of water, the tautomers isocyanuric acid, cyamelide and “insoluble” polymeric cyanuric acid (Figure 3).

Figure 1. Decomposition reactions of endothermic blowing agents: (a) sodium hydrogen carbonate alone; (b) in combination with citric acid; (c) citric acid alone

Figure 2. Decomposition reactions of azodicarbonamide

Figure 3. By-products of azodicarbonamide forming solid residues
The foaming of plastics and elastomers with sulphonydrazides was first reported in the early 1950s [5]. These were a welcome alternative to compounds such as azobis(isobutryronitrile) or diazoaminobenzene, which caused marked discolouration and foamed very early. Since then, toluenesulphonyl hydrazide (TSH) and 4,4’-oxybis(benzenesulphonyl hydrazide) (OBSH) have become established as the most important representatives of the sulphonydrazides. They have much lower decomposition temperatures and more spontaneous decomposition characteristics than azo. Because they are white and their decomposition products in the compound are neutral in colour, they are more suitable for producing light-coloured elastomer foams than azo, which has an inherent yellow colour that disappears only when it is reacted completely. TSH breaks down at approx. 120 – 135°C and gives a gas yield of 140 ml/g. Its reaction, which is much more straightforward than that of azo, is exothermic and it releases nitrogen and water in a first step with the formation of toluenesulphenic acid. In a consecutive reaction, toluenesulphenic acid molecules disproportionate with further elimination of water and dimerisation to form ditolyl disulphide and ditolyl thiosulphonate (Figure 4).

OBSH, the bifunctional sister molecule of TSH, similarly releases approx. 150 ml/g of nitrogen together with water at 160°C. Because of the bifunctionality, high-molecular-weight oligo(oxydiaryl disulphides) and oligo(oxydiaryl thiosulphonates) are formed from the intermediate product oxybis(benzenesulphenic acid) in the disproportionation reaction.

OBSH and TSH are used not only individually but often also as synergists in combination with azo. As well as the heat of reaction coming from the sulphonydrazide blowing reaction, the aryl thiosulphonates formed here also have an activating effect on azo decomposition [6]. The condensation water from the sulphonydrazides also reacts with the isocyanuric acid that is formed as an intermediate from azo, thus reducing the tendency towards cyamelide deposits. Sulphohydrazides and their degradation products also play a part in the kinetics of sulphur crosslinking, where they have an accelerating effect [7]. The possible activation mechanisms are shown in Figure 5.

For the sake of completeness, toluenesulphonyl semicarbazide and 5-phenyltetrazole should also be mentioned as high-temperature blowing agents with decomposition temperatures of between 225 and 250°C. Their use is limited to the foaming of high-temperature thermoplastics such as PC, HIPS and PET. Table 1 provides an overview of the most important exothermic organic blowing agents.

**APPLICATION TECHNOLOGIES**

**Types of elastomer foam**

In principle, solid rubbers can be converted into three types of elastomer foam, which will be discussed and characterised briefly below.

![Figure 4. Decomposition mechanism of sulphonydrazides based on the example of TSH](image)

![Figure 5. Assumed mechanisms of the accelerating action of sulphonydrazides in sulphur vulcanisation: sulphur activation by ring opening, stabilising of activated Zn complex](image)
Older readers will still remember when letters were written on paper and sent through the post after sticking on stamps, which had to be moistened in order to activate the adhesive. For the convenience of their customers, post offices provided small round containers in which could be found a highly porous, open-celled, orange-coloured elastic material imbued with an indefinable mixture of water and the sticky residue from a thousand stamps. This material is sponge rubber [German: Schwammgummi].

Other characteristics, such as its high elasticity, high compressibility with low compressive forces and a relative density of around 0.1 – 0.2, are also useful in devices for cleaning windscreens, in paint rollers and in pipe-cleaning balls (“pigs”). To produce the coarse sponge-rubber structures, rubber is vulcanised in underfilled heated moulds with early foaming, preferably using TSH or OBSH. The preforms are freed from their outer skin and can be mechanically post-treated to increase the open cell structures as required.

### Cellular rubber (closed cell)

If a pipe has to transport hot water with the lowest possible heat loss or a diver has to be protected from the cold, the good insulating properties of closed-cell cellular rubber [German: Zellgummi] come into play. Preferred blowing agents here are TSH and OBSH in combination with azo. To produce cellular rubber in batches, completely filled heated moulds are opened while curing is still incomplete at around t50, resulting in an 8- to 10-fold volume expansion of the vulcanisate. Fine, completely closed, gas- and water-tight cell structures are obtained with relative densities of 0.15 – 0.25, which are under slight pressure and require moderate compressive forces. To produce cellular rubber webs, the unusable upper layers of the expanded sheets are removed.

### Foam rubber – injection moulding and continuous extrusion

Foam rubber [German: Moosgummi] vulcanisates have fine, mixed open- and closed-cell structures with relative densities of around 0.5 – 0.7 and the essential features of a water-tight, closed outer skin, good compression characteristics and low compression set. Add to these their good acoustic damping properties and it is obvious why foam rubber profiles are used to make vehicle body seals. Azo and sulphohydrazides are used for foaming in roughly a 1:1 ratio. Parts are produced by moulding in underfilled heated moulds and expanding until the moulds are 100% filled, or by continuous UHF or salt-bath extrusion.

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<table>
<thead>
<tr>
<th>Structural formula</th>
<th>Substance (abbreviation)</th>
<th>Decomposition temperature in °C</th>
<th>Gas yield in ml/g, air, blowing agents</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Image" /></td>
<td>Azodicarbonamide (AZO, ADCA), yellow-orange powder</td>
<td>205 – 215 (activated grades: 150 – 190)</td>
<td>N₂, CO, NH₃, CO₂</td>
<td>Retarding effect BfR²– no (because of semicarbazide) FDA – yes</td>
</tr>
<tr>
<td><img src="image2" alt="Image" /></td>
<td>Oxybis(benzenesulphonyl hydrazide) (OBSH), white powder</td>
<td>155 -165</td>
<td>N₂, H₂O</td>
<td>Accelerating effect</td>
</tr>
<tr>
<td><img src="image3" alt="Image" /></td>
<td>p-Toluenesulphonyl hydrazide (TSH) white powder</td>
<td>120 – 130</td>
<td>N₂, H₂O</td>
<td>Accelerating effect</td>
</tr>
<tr>
<td><img src="image4" alt="Image" /></td>
<td>Toluenesulphonyl semicarbazide (TSS), white powder</td>
<td>230 – 250</td>
<td>N₂, H₂O</td>
<td>High-temperature blowing agent</td>
</tr>
<tr>
<td><img src="image5" alt="Image" /></td>
<td>5-Phenyltetrazole (5PT)</td>
<td>215 – 225</td>
<td>N₂</td>
<td>High-temperature blowing agent</td>
</tr>
</tbody>
</table>

²Translator’s note: BfR = Bundesinstitut für Risikobewertung (German Federal Institute for Risk Assessment)

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1Translator’s note: German terminology for the various types of foamed rubber does not correspond exactly to the English. Moosgummi is sometimes translated as “sponge rubber” but is not the same as Schwammgummi.
Manufacture

No matter how different the manufacturing routes for elastomer foams may sound, all producers are faced with the same challenge: the timings of the foaming kinetics and the curing kinetics in the compound have to be coordinated if the required cell structure is to be achieved stably and reproducibly. The curing of the elastomer matrix is responsible for fixing the cells. If gas is generated too early, the bubbles can expand without restriction, run into one another and collapse. This results in non-uniform, coarse cell structures, sink marks, craters, poor dimensional stability and, in the case of foam rubber profile extrusion without counter-pressure, irregularities on the profile surface. If the blowing agent reacts later than the curing system, the bubbles in the increasingly cured matrix cannot expand sufficiently, if at all, which results in too high a density or bursting cell structures. Since both the curing system and the blowing system are subject to numerous (mutual) influences within the mixture of substances known as the “rubber compound”, foaming – and especially foam profile extrusion – is one of the most complex manufacturing techniques in the rubber industry, alongside the silanisation reaction in the tyre sector. Individual influences on the overall foaming process are highlighted in Figure 6 (with no claim to completeness). It is clear that compound development must involve a great deal of empiricism and experience in order to ensure uniform foam quality while constantly increasing manufacturing rates in line with the high cost pressures.

Synchronisation of foaming and curing

As already mentioned above, the kinetics of foaming and curing have to be coordinated. Luckily, a number of tools are available for synchronising foaming with curing, which will be discussed in more detail below.

Coordinating blowing agent decomposition temperature with curing process temperature

The well-defined decomposition point of a pure blowing agent can be lowered to a specific level using activators known as kickers. For azodicarbonamide in particular, there is a broad range of combinations available. As well as the sulphohydrazides discussed above, azo can be activated by ZnO and zinc compounds such as Zn benzensulphinate or even ZMBT, and by calcium carbonate, MgO, silica and many other mineral compounds. Sulphohydrazides, on the other hand, are very sensitive to urea or amine compounds, such as the silica activator triethanolamine (TEA) or antioxidants based on diphenylamine (Figure 7).

Blowing agent system

Many of the substances discussed above are already present as components of the formulation and can lead to uncontrollable variations in blowing behaviour in the compound. Constant activation is achieved by a mix of defined quantities of azo and kickers in the form of a blowing agent system. This is then largely independent of the other formulation components in terms of its decomposition behaviour and is, so to speak, “tailored” to the particular manufacturing process. Controlled mixing means that the components are distributed homogeneously and particle-particle contacts, which are important for a reproducible activated blowing reaction, are established (Figure 7).

If powder mixtures are coated with a plasticiser oil, the particle arrangements that form become fixed into clusters by means of the oil shell (Figure 9), bringing about a further increase in the reproducibility of the blowing reaction. Plasticiser can constitute up to 25% of the weight and ensures that the core, which is still
powdery in appearance, no longer releases any dust, thus improving dosing accuracy and occupational hygiene. The latter is currently of particular importance for mixtures based on azodicarbonamide (cf. section 4). A further advantage of the oil-coated blowing agent systems over the pure powders is that they are much more compatible with the rubber compounds and can be incorporated more readily and distributed more evenly—a not inconsiderable contribution to the uniform quality of the foamed products.

Of all the forms of preparation, the most complicated to manufacture but the cleanest and easiest to handle for the processor is the elastomer-bound blowing agent granule. Depending on the blowing agent, up to 75% active substance is kneaded into an elastomer carrier system, which represents an effective encapsulation and phlegmatisation. Transport and storage stability are improved significantly and, in many cases, exothermic products are not subject to explosives legislation restrictions. In mixing rooms where practically all additives are weighed out (semi-)automatically in the form of masterbatches, this is the only form of preparation of any importance.

If compatibility with the type of rubber being processed is good, a blowing agent that has been predispersed in a masterbatch is also much easier to incorporate. Where distribution conditions are difficult (low mix viscosity, short plasticising phases), the use of blowing agent masterbatches is therefore preferred.

Figure 8. Formation of defined blowing agent/activator contacts by targeted powder mixing

Figure 9. Form of blowing agent system: (a) oil coatings fix powder particle arrangements, (b) greater compatibility of coated blowing agents with rubber

Physical properties of blowing agents—determining gas yield, decomposition kinetics and particle size distribution

Users are primarily concerned with two properties of a blowing agent: how much gas is released and at what temperature? In a simple method for determining these properties, the sample material is weighed into a test tube, which is then connected via a flexible silicone hose to a horizontally clamped gas syringe and placed in a heating block.

To measure the decomposition temperature, the heating block is heated up continuously and the temperature at which the gas syringe spontaneously starts to move is noted.

To determine the gas yield, the heating block is set to a constant temperature before the measurement begins. The test tube, prepared as outlined above, is placed in the heating block. When gas generation has concluded and the gas syringe has come to rest, the volume of gas produced is reduced by the inherent expansion of the air that is present in the system, which was measured beforehand, and related to the amount of substance weighed in. The gas yield determined in this way represents the maximum amount of gas that can be liberated at a predetermined temperature in practice, irrespective of the time taken. In the case of endothermic blowing agents, the time needed is always longer than for exothermic blowing agents. If the gas generated is not collected directly as described above but determined by displacement of a water column, the values are around 20–30% lower.

Modern methods for characterising the thermal behaviour of a material are thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Both methods require sophisticated equipment, offering a sound basis for reproducible results with very small sample quantities and a high level of automation. Introduction of these methods is very time-consuming owing to the development work needed in terms of sample weight, temperature program, flushing gas, sample preparation and evaluation.

In TGA, a sample of approx. 5 mg (accurate to 1 µg) is weighed into a ceramic sample pan. The sample pan is placed on a precision balance, the heart of the instrument, e.g., using an automatic sample changer. Multiple thermocouples are positioned directly above the sample and the balance and sample are placed in a furnace which is capable of running a wide range of temperature programs. Measurements at a constant heating rate of 10 K/min are usual, but isothermal phases and different rates of heating are also possible. While the sample is being heated (e.g. from 30–300°C), the current mass of the sample is constantly being determined and plotted against the temperature. This allows all processes taking
place in the sample connected with gas evolution, and therefore loss of mass, to be assigned very accurately to a specific temperature range. In this way, information is obtained on the overall decomposition behaviour of a sample in the selected temperature range. Apart from the decomposition temperature, other parameters that can be specified for quality control are mass losses up to certain temperatures, which are comparable with the known gas yield in terms of the information provided.

In DSC, a small sample quantity (approx. 5 mg) is placed in an aluminium sample pan and an empty pan is placed in the sample chamber as a reference. The two pans are subjected to a predefined temperature program in the furnace while recording the amount of heat that has to be supplied to or dissipated from the sample in order to equalise the sample and reference temperatures. In this way, changes in enthalpy of the sample are plotted against temperature. This measuring principle enables a distinction to be made between endothermic (energy-absorbing) and exothermic (heat-releasing) processes in the sample. Using this method, it is possible to determine the specific enthalpy of decomposition, i.e. the amount of heat absorbed or given off in the decomposition of one gram of blowing agent.

Apart from the thermal characteristics of blowing agent powders, their particle size is also of particular interest since it has a direct effect on the foam structure in a foamed elastomer. A fine particle size powder always produces finer bubbles while a coarser grade of powder ensures larger cells and decomposes more slowly than the fine powder, which has greater surface activity. One common method is laser diffraction analysis, in which either the substance is atomised as a dry powder and passed through a laser beam at a 90° angle or alternatively the powder can be suspended in a liquid and tested in a measuring cell. Particles of different sizes deflect the laser beam differently in accordance with Rayleigh’s Law and lead to a typical diffraction pattern, which can be converted to a particle size distribution. Characteristic values such as the D50, D90, and D100 values can be obtained from this, representing the maximum size of 50%, 90% or 100% of the particles. For example, D50 = 3.8 µm means that 50% of the particles have a diameter ≤ 3.8 µm.

AZODICARBONAMIDE – THE REGULATORY POSITION

As outlined in section 2, for decades azodicarbonamide has been the most important chemical blowing agent in terms of volume and could be described as the “workhorse” for thermoplastic and elastomer foams. As well as its chemical properties, its effects on health have also been documented over the years. Ten years ago, azo was banned from the production of foamed seals in contact with foodstuffs because semicarbazide can be formed from its breakdown products. As early as 1994, azodicarbonamide was categorised as a respiratory allergen as a precautionary measure after an increase in asthmatic complaints was observed under certain conditions in production workers handling powdered azo in the UK in the 1980s. However, all user industries in Europe were equally surprised when in 2012, on the basis of an official submission from Austria [8], the ECHA included azo in the Candidate List of substances of very high concern (SVHC), so that it now ranks alongside toxic lead, chromium, cadmium and arsenic compounds as well as various organic compounds classed as carcinogens or teratogens. Since then, industry experts have been puzzling over the reasons behind this SVHC nomination. There is no proof of the occurrence – let alone a broad distribution – of azo-related occupational asthma in the processing industries (not only rubber but also blowing agent masterbatches, PVC pipes, wallpaper etc.), partly because of a lack of data [9]. Moreover, when members of the public handle foamed plastics in their daily lives as end users, they do not come into contact with azo-containing dust, since any azo that might still be present is firmly bound in the polymer matrix. By way of example, investigations into azo-foamed CR and SBR vulcanisates carried out by an accredited laboratory on behalf of Lehmann & Voss showed no detectable residual azo contents in either case, with a limit of detection of 0.02%.

Furthermore, in contrast to the situation in the USA, baked goods produced in Europe are not permitted to contain up to 45 ppm azodicarbonamide as a flour treatment agent. European flour dust allergies and flour dust explosions cannot therefore be linked to azo. (At this point, the author breathes a sigh of relief that wheat flour is regarded as a natural product and so does not come under the jurisdiction of the ECHA. The socio-economic consequences of placing flour on the SVHC list, and particularly of the eventual ban on bakery products that could entail, would be devastating.)

The azo/SVHC sceptics’ strongest argument may be taken from the result of a current skin sensitisation study by the European ADCA Task Force, however. According to this study, it is generally considered in occupational health that a respiratory allergen is always a skin sensitiser, but no skin-sensitising effect could be found for azodicarbonamide [10].

Once azodicarbonamide had been classed as an SVHC candidate, the ECHA rapidly placed it on the priority list of substances selected for inclusion in Annex XIV – Authorisation List. The inclusion of azodicarbonamide in Annex XIV would mean that all azo users or their suppliers would have to apply for a cost-intensive, time-limited authorisation for every application in which azo is used. The committee of experts of the Member States is meeting in December 2015 to discuss this and, possibly,
to establish the so-called “sunset date” up to which azo can continue to be used without authorisation. This will require unanimous resolutions by the committee members. The committee has been able to obtain political support in its efforts to reach consensus: the German Bundesrat recently demanded “... for authorisation procedures under chemicals legislation, greater transparency and plannability of these procedures to protect SMEs from economic losses”. It also requested that the EU “dispense with authorisation procedures if a substance represents a risk only in the workplace and this risk can be controlled by current industrial safety regulations.” [11]

What are the options for SMEs if azodicarbonamide should nevertheless become subject to authorisation?

The use of dust-free azodicarbonamide preparations is, in any case, a sensible measure in terms of occupational hygiene and improvement of mixing results, and can continue without any additional regulatory effort until a sunset date is reached. Analysis of azo traces in random samples of vulcanisates could be performed at reasonable cost and would safeguard the rubber producer as well as the amenable downstream user.

Should the requirement for authorisation come into force, there is the danger that influential downstream users, such as the automotive industry, might expect their suppliers to avoid all Annex XIV substances in components. On the other hand, azodicarbonamide is unique in its foaming kinetics, gas yield and other properties and there is currently no substance on the horizon that could replace azo on a 1:1 basis. Anyone wishing to utilise the time up to the sunset date to develop alternative, azo-free formulations would therefore have to use the accelerating, much earlier-foaming sulphohydrazides as the main components. There are no known Retarding additives that would shift the sulphohydrazide foaming reaction into the same temperature range as azo. OBSH and TSH would therefore need the vulcanisation system to be readjusted. Even this scenario does not protect the user from the possibility that new toxicological assessments and classifications for sulphohydrazides could come to light under the REACH procedures, which would put the results of this development work at risk.

Apart from sulphohydrazides, expandable microspheres may represent another alternative. These consist of low-boiling hydrocarbons encapsulated in a spherical shell of solvent-resistant polymer. When they are heated, the shell softens and the material inside boils and expands the shell. This clear mechanism means that handling is relatively non-critical. Various sphere diameters, blowing fluids and shell softening points are available, offering the possibility of adaptation to individual applications. On the negative side, there is the question of whether expandable microspheres can provide sufficiently high blowing pressure in rubber compounds as well as the issue of VOCs arising from the low-boiling compounds. Expandable microspheres have already been used in the plastics sector, e.g. for foaming PVC underseal in vehicle construction. As well as the powders, polymer-bound masterbatches are also available [12].

If low-boiling substances like those found in expandable microspheres are to be avoided, there is also the possibility of using hollow glass microspheres (HGMs) as lightweight fillers for density reduction. These are made of special minerals and are stable under pressures of up to 2000 bar with densities from 0.6 down to 0.12. With D₅₀ particle diameters of 20 – 40 µm, HGMs act as inactive fillers allowing high filler levels to be achieved even in soft compounds. On the plus side are the high mechanical and chemical stability and the simple mechanism of action of HGMs, while on the minus side are the relatively large transport volumes resulting from their density and the handling issues relating to dust. Because of the high level of dust generated, oil-coated HGM preparations have been developed which improve handling and mixing characteristics [13]. However, the relatively high price of HGMs is currently a barrier to their broader application.

At present, there is no ideal route to an azo-free future. Lehmann & Voss & Co. will continue to monitor the situation by participating in the European ADCA Task Force and will work on developing solutions if this is what the user industries want.

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