Odour absorption from activated zinc ricinoleate

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Smell is one of the five most important senses (sight, hearing, touch and taste), allowing us to perceive life in its entirety. The perception of smell is a very complex process including the excitation of specialised receptors located in the human nasal cavity, and signal transmission to the brain. Smells are caused by volatile chemical compounds, which can often be recognised even when present in low concentrations.

Odour plays an important role in our lives. It evokes emotions and memories, changes cognitive and physical abilities, and of course affects relationships between people. For this reason, the problem of odours has been preoccupying scientists and industrial developers for many years.

We have to consider the subjective perception when talking about pleasant and unpleasant odours. Acceptance of unpleasant odours can be determined by averaging the opinion of the population. The main source of malodours are sulfur and nitrogen containing molecules, such as allicin – garlic, felinine - cat urine, hydrogen sulfide - rotten eggs, ammonia – urine, indole and skatole – fecal, cadaverine and putrescine – rotting flesh, nicotine – tobacco and so on. In addition, there are other odorous substances that are responsible, for example for smell of sweat - isovaleric acid, rancid oil - butanoic acid, tobacco smoke - acetaldehyde etc. In everyday life the number of unpleasant odours originated from non-sulfur and non-nitrogen containing molecules is very limited.

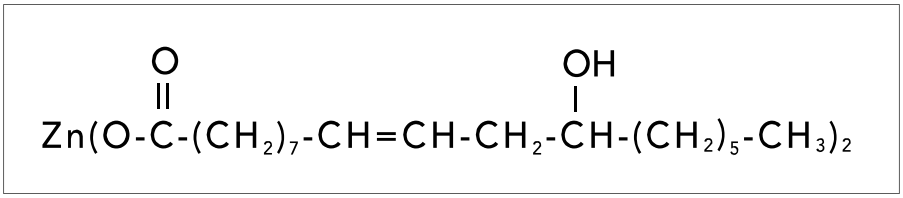

Figure 1: Chemical formula of zinc ricinoleate.

The most common solution to 'change' unpleasant odours is the use of fragrances. Such mixtures release a pleasant scent and are able to cover unpleasant odours. This masking is not always effective and after dispersing the fragrance, unpleasant odour molecules will be predominant in the atmosphere again.

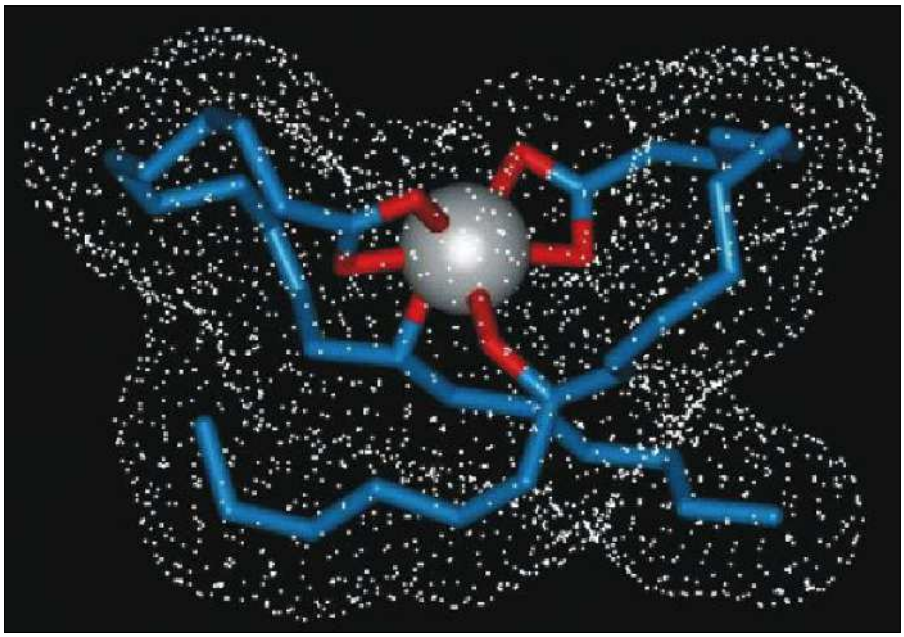

Figure 2: Three-dimensional model of zinc ricinoleate molecule.

Odour absorbers

Another strategy to fight against bad odours is the development of odour absorbers. A lot of effort and scientific work has been done and this trend is still growing. Odour absorbers are substances that entrap odour-causing molecules and hold them for a long time. The most famous absorbers include activated carbon, zeolites (aluminosilicates), cyclodextrins and zinc ricinoleate. Macro or micro molecular structures of the first three substances resemble cavities, where absorption of odour molecules occurs. This process is in most of these cases not selective. Besides substances with unpleasant odour, also welcoming molecules like perfume components, can be absorbed. An additional difficulty when using activated carbon and zeolites in personal care or household products is their insolubility in water.

Zinc ricinoleate

Zinc ricinoleate has already been established in the area of industrial applications as well as in a wide range of personal care products and household chemicals. Its potential for absorption is based on the ability of divalent zinc atom to form stable complexes of a high degree of coordination with molecules containing electron-donating groups or atoms like nitrogen (N) and sulfur (S). The coordination number usually corresponds to four or six, which means, each zinc ricinoleate molecule can bind up to three suitable

molecules. This makes zinc ricinoleate very effective to absorb unpleasant odours, which are often caused by nitrogen and sulfur containing molecules, namely amines, ammonia, mercaptans, thio esters, hydrogen sulfide, low molecular weight organic acids, etc. It is important to note that pleasant scents, such as fragrances, mainly containing ester, aldehyde or aromatic groups, will not be affected by adsorption.

Figure 1 shows the molecular structure of zinc ricinoleate. This molecule consists of a zinc atom and two ricinoleic acid moieties and can be synthesised by neutralisation of ricinoleic acid with zinc oxide. Both starting materials are natural substances. Zinc oxide can be obtained from mineral sources, and ricinoleic acid derives from castor oil triglycerides (content of about 90%). Thus, zinc ricinoleate is a natural molecule obtained from renewable sources. Today, it is one of the important parameters to choose raw materials.

The modern requirements for environmental friendliness makes zinc ricinoleate, due to its high biodegradability, a very attractive component for certified products.

The use of pure zinc ricinoleate is in various areas still limited or complicated. It is a waxy substance with a melting point of about 80 °C, which is insoluble in water and not active in terms of odour removal.

The three-dimensional model of the zinc ricinoleate molecule (Fig 2) shows the formation of an intramolecular complex of the zinc atom with free electron pairs of oxygen atoms from hydroxyl groups of ricinolic acid residues of the same molecule. The molecule of pure zinc ricinoleate is a hydrophobic symmetrical sphere. Interactions between hydrophilic groups and water molecules are very limited that leads to poor water solubility of the substance. Due to the electrostatic shield provided by the oxygen atoms of the ligands, Zn^{2+} is protected against nucleophilic attacks of other molecules that explains the low efficiency of using pure zinc ricinoleate as an odour absorber.

Zinc ricinoleate activation

Computer simulations (Fig 3) showed that the zinc ricinoleate molecule can be activated by interaction with a chelating agent such as methylglycinediacetic acid trisodium salt (MGDA).

$$Zn(Ri)_2 + MGDA \rightleftarrows (Ri)_2 Zn \text{ --- } MGDA$$

During the formation of the complex, the ricinoleic acid residues unfold and the hydroxyl groups are released and oriented to the water phase, providing good solubility of the complex. Re-complexation

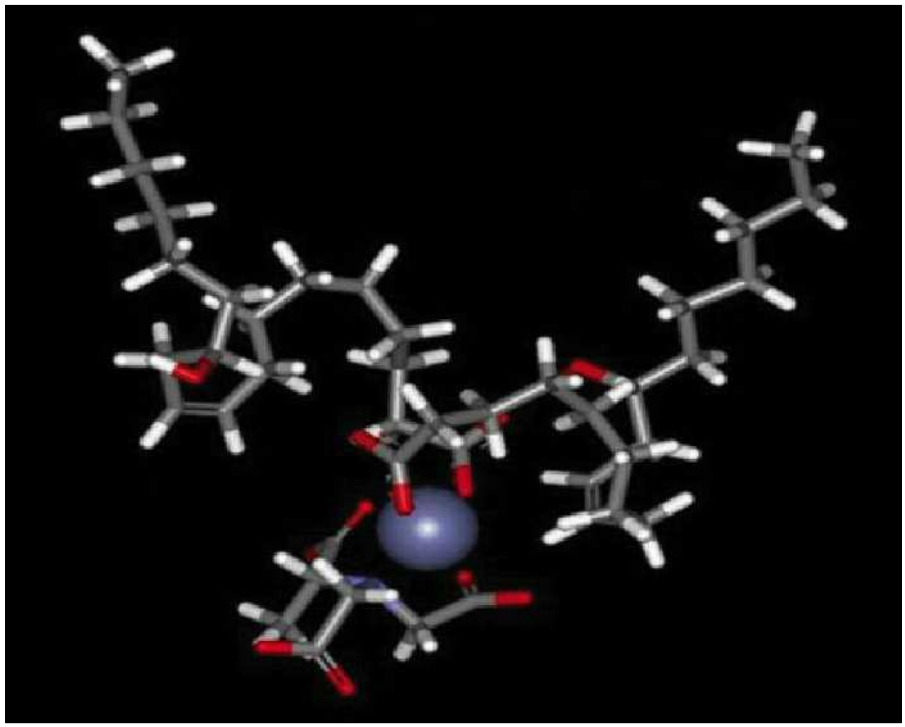

Figure 3: Molecular simulation of the interaction of zinc ricinoleate and MGDA.

Table 1: The Polyfix products range.

Polyfix ZRC 25 GP	Aqua, Zinc Ricinoleate, Tetrasodium Glutamate Diacetate, Propanediol
Polyfix ZRC 25 MB*	
Polyfix ZRC 25 EC	Aqua, Zinc Ricinoleate, Tetrasodium Glutamate Diacetate, Propylene Glycol
Polyfix ZRC 50 TB	Zinc Ricinoleate, Laureth-3, Tetrahydroxypropyl Ethylenediamine, Propylene Glycol
Polyfix ZRC 30 MT	Water, Zinc Diricinoleate, Chelating Agent, Alcohol Ethoxylated

*Mass Balance

is possible because the interaction of MGDA and zinc ricinoleate is weak. Since the formation of a complex is a reversible process in a dynamic equilibrium, its geometry is constantly changing. The zinc atom becomes available for attack by other nucleophiles. The interaction between the zinc atom and molecules containing nitrogen or sulfur is so strong compared to the interaction with a chelating agent that after recombination such complexes remain stable even at high temperatures.

Computer simulations confirm that the chelating agent is capable of serving as a solubiliser and activator for zinc ricinoleate.

A series of water-soluble odour absorber concentrates

Using this knowledge, Schill + Seilacher GmbH has developed the Polyfix series of highly effective, water-soluble odour absorber concentrates (Table 1).

An additional advantage of this activation mechanism is the ability of Polyfix products (now referred to as 'the odour absorber concentrates and '30 MT' / '25 GP' for Polyfix ZRC 30 MT / Polyfix ZRC 25 GP) to absorb molecules efficiently and quickly from the gas phase. Activated zinc ricinoleate as a soap, possesses surfactant properties. Its molecules will self-assemble at the surface of the solution (Fig 4). The geometry of the complex allows the zinc atom to capture molecules of unpleasant odours from the air as soon as they are close enough for interaction.

Performance tests

Various tests of the effectiveness of the odour absorber concentrate range and finished products including the odour absorber concentrates verify the high performance of the new materials. A test regarding absorption capacity of the odour absorber concentrates against different types of compounds with unpleasant odours was carried out as follows:

Two Petri dishes were placed next to each other under a large hood. The concentration of molecules with an unpleasant odour in the atmosphere of this closed system was measured either in the presence or absence of the odour absorber concentrates.

For each 'bad smell' substance, three experiments were carried out. In each of

them, one Petri dish was filled with certain amounts (the same for all three experiments) of a compound giving an unpleasant odour. The measurement of its gas concentration was carried out 10 minutes after closing the system. In the first experiment, the second Petri dish remained empty. In the second test, it was filled with water. In the final third, a certain amount of the solution of the tested odour absorber, for instance diluted odour absorber concentrate (30 MT), was added.

The use of a 30% diluted solution of the odour absorber concentrate (30 MT) for the absorption of nitrogen and sulfur containing compounds of above system shows a reduction of the diethylamine concentration in the system from 200 to 74 ppm, i.e. more than 63% (Fig 5). The absorption efficiency of ethanethiol is even higher, almost 77%, herewith the concentration decreases from 35 to 8 ppm.

Figure 6 shows the ability of two market products to absorb hydrogen sulfide. A cream soap and a detergent containing another type of odour absorber, have been tested without and with the addition of 30 MT. For the first product, the concentration of hydrogen sulfide could be decreased by 6.5 times from 400 to 60 ppm by using 30 MT. Absorption rates of the second product in the presence of 30 MT improved from 50% to almost 100%, that only 12 ppm of hydrogen sulfide remained in the system.

Comparison of the performance of the odour absorber concentrate products (25 GP and 30 MT) and a competitive product also based on zinc ricinoleate for the absorption of ammonia, hydrogen sulfide and acetic acid confirms the special effectiveness of Schill+Seilacher GmbH products. Efficiency was calculated by the formula:

$$\text{efficiency (\%)} = 100\% - \frac{\text{residual concentration of "bad smell" substance in the presence of an odor absorber}}{\text{initial concentration of "bad smell" substance, "Blank"}} \times 100\%$$

As shown in the diagram (Fig 7), the efficiency of the odour absorber concentrate products for ammonia absorption reaches 65%, while the competitive product gives 45%. Hydrogen sulfide is removed by 25 GP and 30 MT by 80% and 90%, respectively. But for the competitive product, 68% can be achieved. Only in the case of acetic acid, the efficiency for all three products fluctuates within the measurement error.

Schill+Seilacher GmbH developed a basic deodorant formulation with 25 GP (Table 2). A similar test was carried out for this formulation with and without the odour absorber concentrate as well as for two commercial available deodorants containing zinc ricinoleate (Fig 8). The presence of zinc ricinoleate in the tested

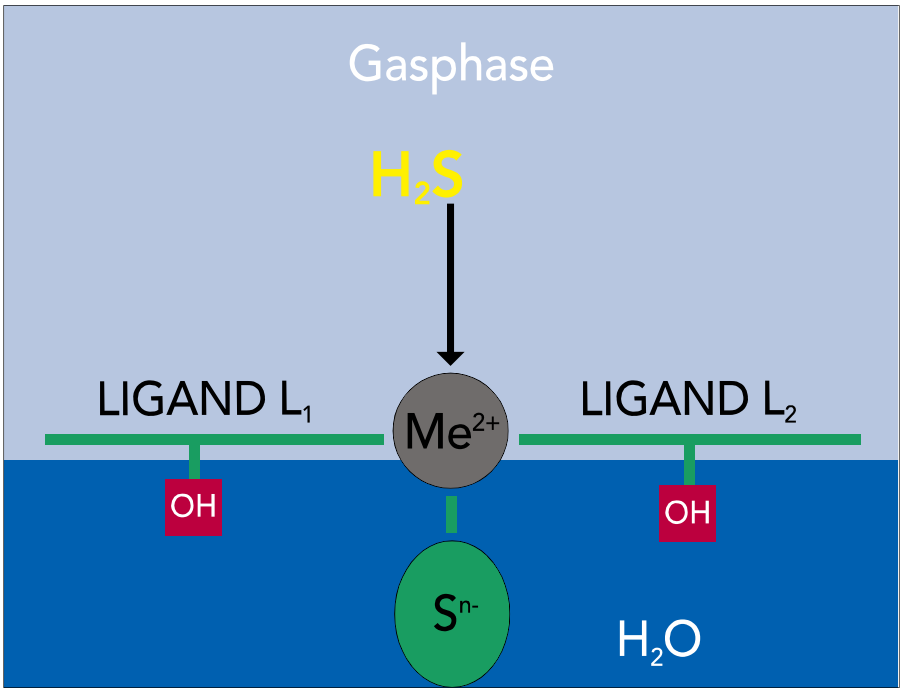

Figure 4: Self-assembly of the complex on the surface of the solution.

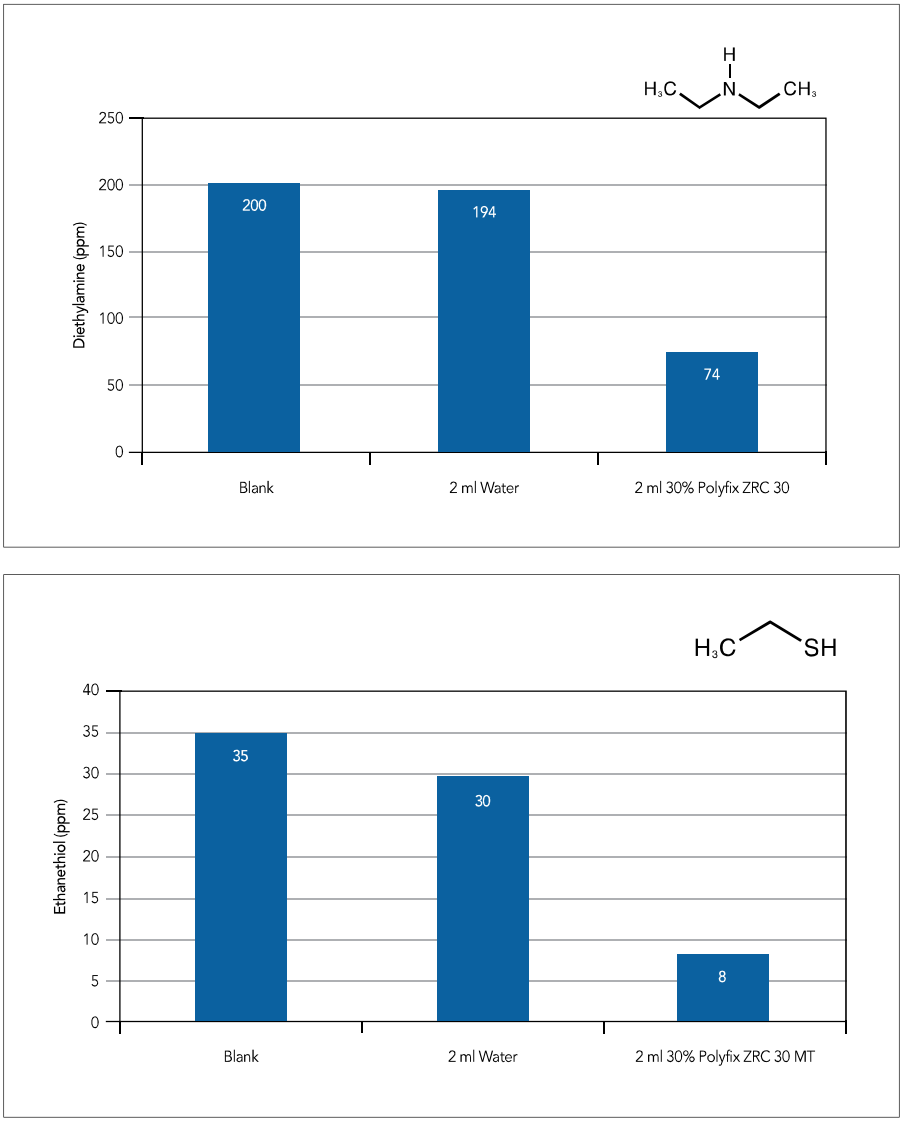

Figure 5: Absorption of diethylamine (top) and ethanethiol (bottom) by 30% diluted solution of Polyfix ZRC 30 MT.

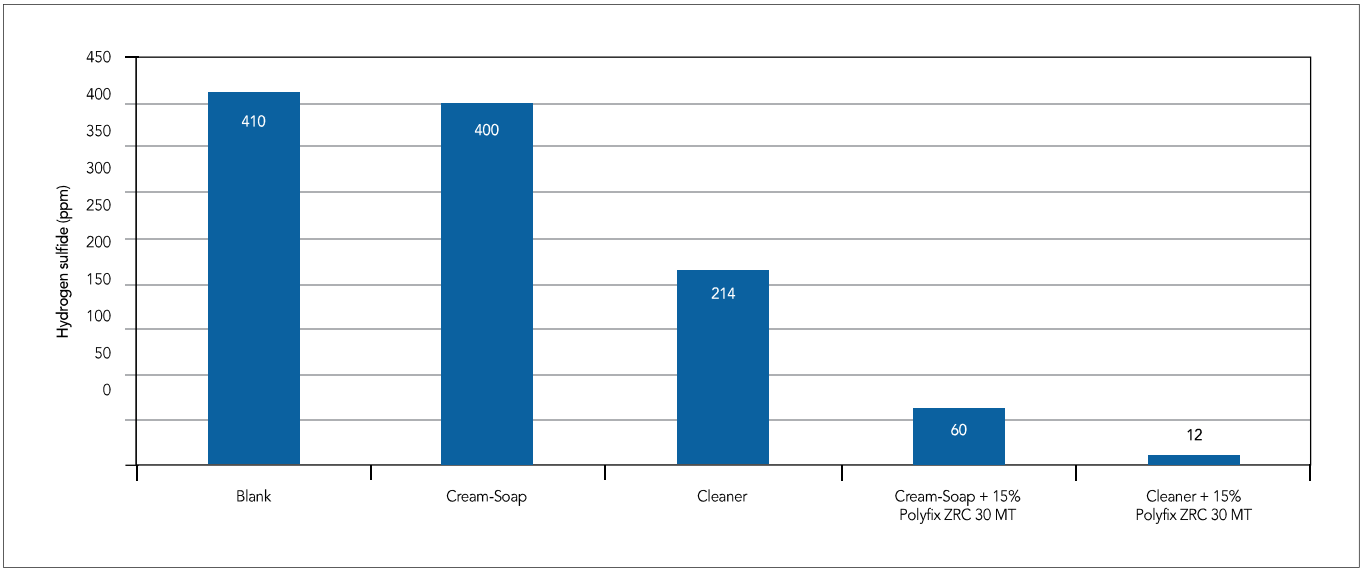

Figure 6: Absorption of hydrogen sulfide by two market products without and with the addition of 15% Polyfix ZRC 30 MT.

formulation provides a significant change in the ability of the deodorant to absorb various types of unpleasant odours.

Comparison of the developed product with market products shows that the formulation containing the odour absorber concentrate 25 GP has an efficiency comparable to product 1. The absorption of hydrogen sulfide and acetic acid is better compared to product 2. The zinc concentration in both commercially available products was 3-4 times higher than in the product containing the odour absorber concentrate (25 GP).

It should be noted that the increased efficiency of product 2 upon absorption of ammonia can be explained by neutralisation of ammonia due to relatively acidic pH 5.5 of product 2, but not because of the higher efficacy of odour absorber.

The activation of zinc ricinoleate plays an important role in the interaction with odour molecules as shown by the deodorant formulations. To achieve the desired effect, significantly less odour absorber concentrate is needed compared to a competitive product based on non-activated zinc ricinoleate.

25 GP was tested for its efficacy against artificial sweat by the independent Hohenstein Institute which is specialised in the detection of odours. Sweat odour intensity was evaluated in comparison to a reference by trained panellists using an olfactometric sampling unit. It was shown that the initial intensity of unpleasant odour will decrease from 'extremely strong' to 'weak - very weak' when using 10% solution of 25 GP (Fig 9).

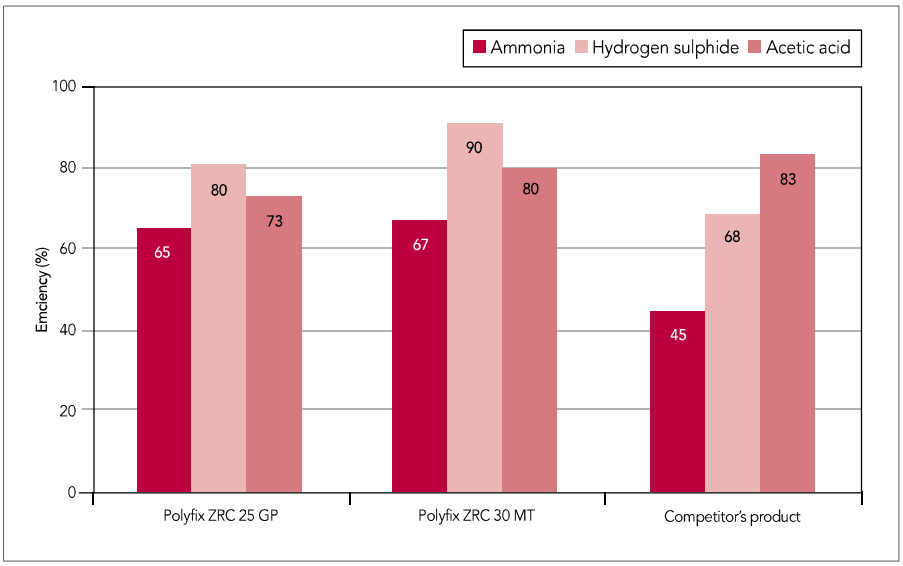

Figure 7: Efficiency (%) of 5% solutions of Polyfix ZRC 25 GP, Polyfix ZRC 30 MT and competitor's product regarding absorption of ammonia, hydrogen sulfide and acetic acid.

The results of a statistical survey (24 men and women) about the effect of 30 MT on various odours are shown in Figure 10. Testers had to evaluate odour intensity after spraying of an odour containing sample with diluted odour absorber concentrate solution on a scale of 1 to 6. The maximum odour intensity of the untreated substance was set to value of 6 as benchmark. This survey confirms the superior performance of 30 MT.

On one hand 30 MT fights against unpleasant odours (smells of garlic, onions, fish, cigarettes, ammonia, butane and thioglycolic acid) and on the other hand it is perfectly compatible with perfumes and fragrances whose intensity remained almost unaffected after processing the odour absorber concentrate.

Table 2: Basic formulation of deodorant roll-on "Perfect Polyfix" with Polyfix ZRC 25 GP

	Ingredients	Weight %
A	Aqua	90.7
B	Sucraclear HC-3 (Natural thickener)	1.0
C	Propanediol (Moisturizing agent)	1.0
	Probiophyte Fresh (Mild preservative)	2.0
	Polyfix ZRC 25 GP (Odour absorber)	5.0
	Perfect Day (Fragrance)	0.3
D	Citric acid	qs to pH = 7.8 - 8.3

Procedure: Heat Part A up to 70°C, maintain temperature and add Part B while stirring. Mix until preparation appears homogenous. Cool down to room temperature while stirring. Add Part C in listed order. Adjust pH with Part D.

Application fields

The odour absorber concentrates can be used in many areas of our lives. With regards to industrial use it is found in different types

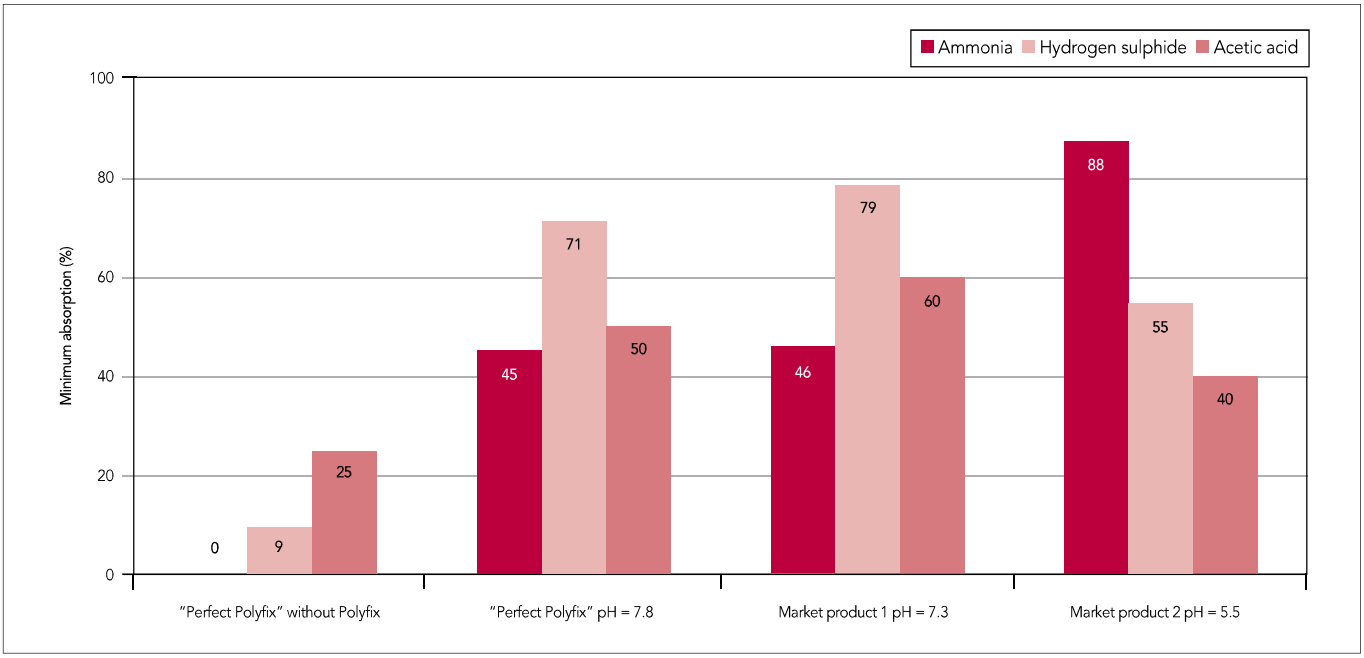

Figure 8: Efficiency (%) of deodorant roll-on "Perfect Polyfix" without and with Polyfix ZRC 25 GP and two market products containing zinc ricinoleate regarding absorption of ammonia, hydrogen sulfide and acetic acid.

of filters, detergents, freshing and spraying systems, for example at chemical plants, fish processing factories or garbage and industrial waste storage enterprises. The odour absorber concentrate is often used as an ingredient in personal care products such as deodorants (spray, roll-on, stick), gels and foot creams, intimate hygiene products and even oral care products, like mouthwash or toothpastes. Products made with the odour absorber concentrate received the widest use in household applications in detergents, especially against smell of tobacco and animals, fabric treatments, fresheners of clothes and shoes, upholsteries, curtains, carpets and the interior of cars, and also in detergents for laundry, especially sportswear. The odour absorber concentrate can be applied to liquid kitchen soaps as well as for pet shampoos. In some cases, the odour absorber concentrate effectively neutralises unpleasant odour of components in mixtures, for instance thioglycolic acid in products for depilation, permanent waves or hair straightening. These examples show the universal range of applications of these products.

Conclusion

Summarising all the above, it can be clearly concluded that Polyfix products from Schill+Seilacher GmbH are the most effective absorbers of a wide range of unpleasant odours that will not affect perfumes. These concentrates of activated zinc ricinoleate are cold processable and can be easily incorporated into various types of systems. Products are environmentally friendly whereas Polyfix ZRC 25 GP, Polyfix ZRC 25 MB and Polyfix ZRC 25 EC are COSMOS approved. PC

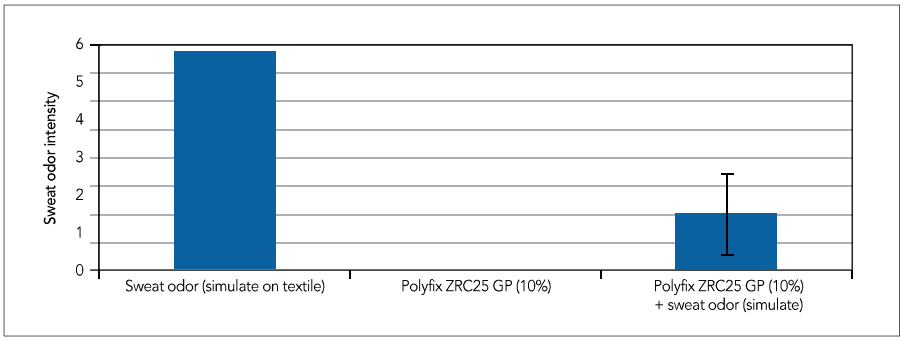

Figure 9: Absorption of artificial sweat odour by 10% solution of Polyfix ZRC 25 GP. (Intensity: 6 - extremely strong, 5- very strong, 4 – strong, 3 – distinct, 2 - weak, 1 – very weak)

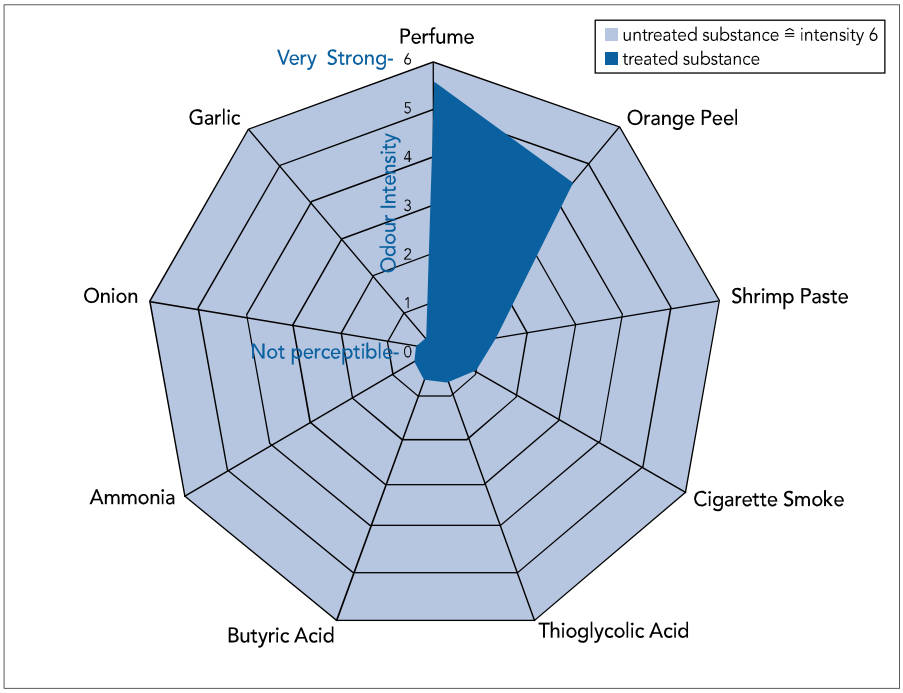

Figure 10: Statistical survey with 24 male and female subjects about the effect of diluted Polyfix ZRC 30 MT on various odours - clockwise arrangement of odour intensity.