Brighten the appearance of pet food

by Dr. Roland Beck

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Insoluble white colorants and opacifiers, whitening pigments such as titanium dioxide, have long been used to modify the appearance of food and pet food products. The key properties of such whitening pigments are to increase the opacity of a translucent matrix, e.g. a sauce or gel, or to brighten up an otherwise darker-coloured product, to produce a product with more appealing visual characteristics. The safety of titanium dioxide has been challenged by authorities for some time now, and there is a need to replace it with a safe and natural alternative.

What does the market need?

Due to the recently published opinion by ESFA (May 2021) that titanium dioxide is no longer perceived as safe, public perception and political opinion are likely to remove this product from the list of permitted additives. Replacement of titanium dioxide by a safe and natural whitening pigment is therefore a must for all producers.

What are the requirements for a whitening pigment alternative?

- Recognised as safe and globally permitted
- Whitening and opacifying effect in a wide range of matrices
- Temperature, pH and storage stable
- Inertness towards other ingredients such a vitamins, flavours or colours
- No unwanted sensory impact
- Out of the nano size range
- Consumer recognition of the naturalness of the product and manufacturing process
- Acceptable cost in use

Understanding the physics of whitening and opacifying pigments

In contrast to true colourings whose function is based on the absorption of visible light, the function of white colorants is based on the scattering of light. The theory of scattering of electromagnetic radiation is based on the fundamental work of Gustav Mie (Mie 1908), which developed a function to relate the optical cross section relative to the geometric cross section of a single particle (Equation 1).

$$Q^{sca} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2 + |b_n|^2)$$

Equation 1: Relative scattering cross section, Q^{sca}, of a particle with the size parameter $x = 2r\pi n_b/\lambda$ and the Mie coefficients $a_n = \frac{\Psi_n(x)\Psi_n'(mx) - m\Psi_n'(x)\Psi_n(mx)}{\zeta_n^{(1)\prime}(x)\Psi_n'(mx) - m\zeta_n^{(1)\prime}(x)\Psi_n(mx)}$ and $b_n = \frac{\Psi_n'(x)\Psi_n(mx) - m\Psi_n(x)\Psi_n'(mx)}{\zeta_n^{(1)\prime}(x)\Psi_n(mx) - m\zeta_n^{(1)}(x)\Psi_n'(mx)}$ with Ψ and ζ representing the Riccati-Bessel functions and m the ratio of the particle refractive index n_p and of the surrounding medium n_b.

From a practical point of view, however, the scattering ability of a large number of particles embedded in a matrix is required for evaluating the whitening effect of a colorant. Weber (Weber 1961) has modified Mie's equation by relating it to the totality of all scattering particles of a given volume concentration in a defined volume (Equation 2) introducing the term scattering coefficient ($N_V S$) for this.

$$N_V S = \frac{3}{2} C_V \frac{Q^{sca}}{2r}$$

Equation 2: Scattering coefficient $N_V S$, whereby Q^{sca} is the relative scattering cross section, $2r$ is the particle diameter and C_V is the volume concentration of all particles in the medium.

Further transformation of Equation 2 leads to the concentration-independent scattering efficiency of a whitening pigment, S_{sca} (Equation 3), which allows the comparison of the whitening power of pigments with different refractive indices and particle sizes in matrices with different optical densities.

$$S_{sca} = \frac{3\pi}{2x} Q^{sca}$$

Equation 3: Scattering efficiency, S_{sca}, for the totality of all particles

In Figure 1 the scattering efficiency, S_{sca}, is plotted in relation to the particle diameter ($2r$) and the optical contrast ($n_{p/}\, n_b$) in an aqueous matrix with n_b = 1.33 at a wavelength of the incident light of λ = 560 nm. The higher the optic contrast the higher the scattering efficiency becomes, provided the particle size is right. There is a clear optimum for any given particle diameter and optical contrast, which follows a 1/x relation. At the optimal particle size the scattering efficiency increases with the optical contrast. Outside this optimal particle size range the scattering efficiency reduces significantly, which is true for particles smaller and larger than the optimal size.

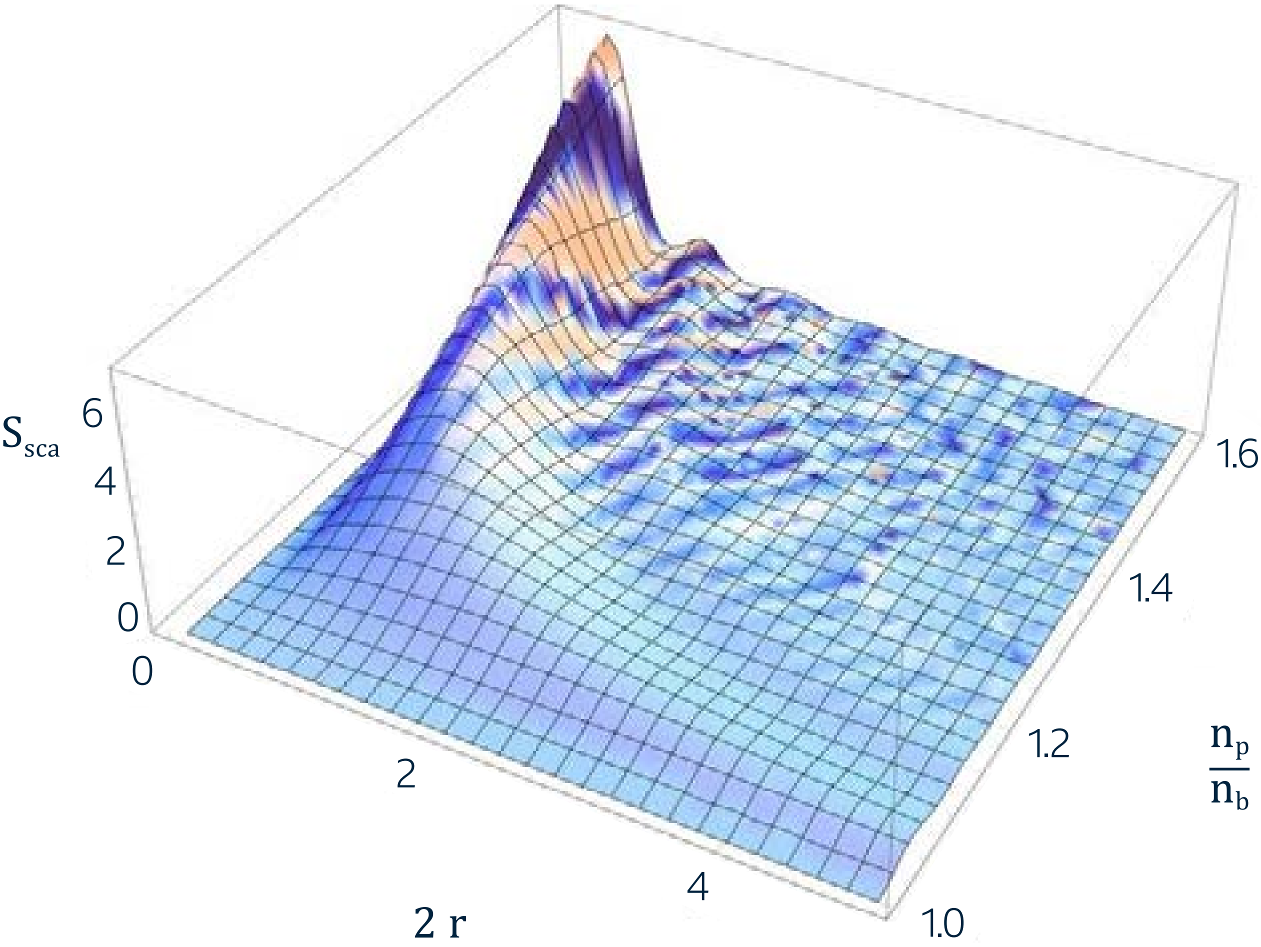

Figure 1: Scattering efficiency of pigments in relation to their particle size and the optical contrast at an incident wavelength of λ = 560 nm

The optical contrast range for titanium dioxide, due to its outstanding high refractive index, is always in the range of $n_{p/}\, n_b$ > 1.6, requiring a narrow particle size distribution with an average particle size of 0.2–0.3 µm. Under these assumptions titanium dioxide is an extremely effective whitening and opacifying pigment.

All other organic or inorganic insoluble pigments will produce a significantly lower scattering efficiency due to their lower refractive index and in consequence the lower optical contrast, which will be in the range of $n_{p/}\, n_b$ = 1.1–1.2 for food and pet food products. In Figure 2 the scattering efficiency at the optimal particle size is plotted against optical contrast at a wavelength of λ = 560 nm. The scattering efficiency is in an approximately linear relation with the optical contrast.

Since the refractive index of substance is a physical constant, it is of utmost importance to know the optimal particle size for being able to produce a whitening pigment with the highest whitening and opacifying effect in a given matrix. Several approaches exist for solving this task by for instance Weber, Lothian (Lothian 1951) and Jaenicke (Jaenicke 1956). All of them produce very similar results (Figure 3). Certainly, the simplest solution is the one by Weber, which relates the wavelength of the incident light to the difference in refractive indices of the pigment and the matrix (Equation 4).

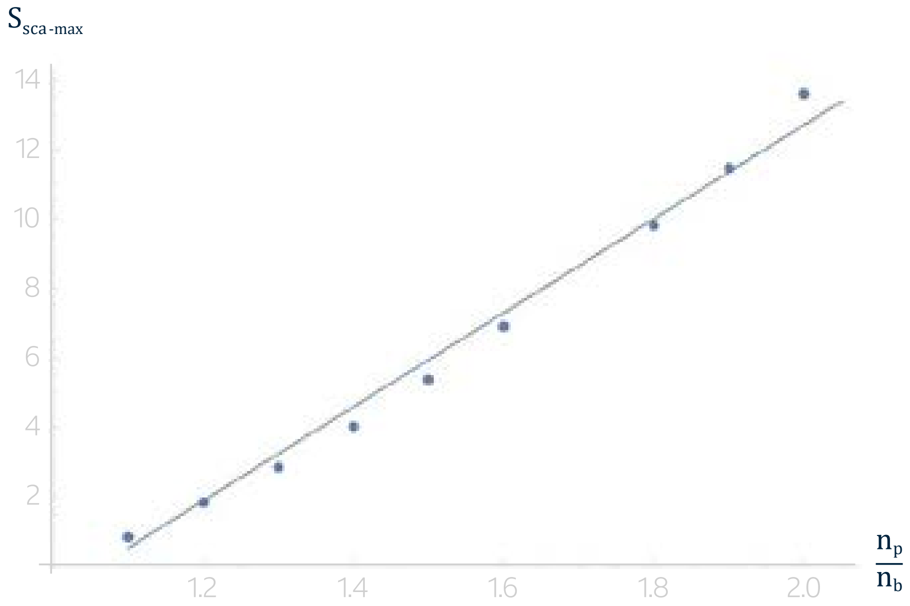

Figure 2: Scattering efficiency of particles at the optimal particle size for scattering in relation with the optical contrast at a wavelength of $\lambda = 560$ nm

$$2r_{opt} = 0.475\,\lambda\,/(n_p - n_b)$$

Equation 4: Optimal particle size formula of Weber for scattering efficiency

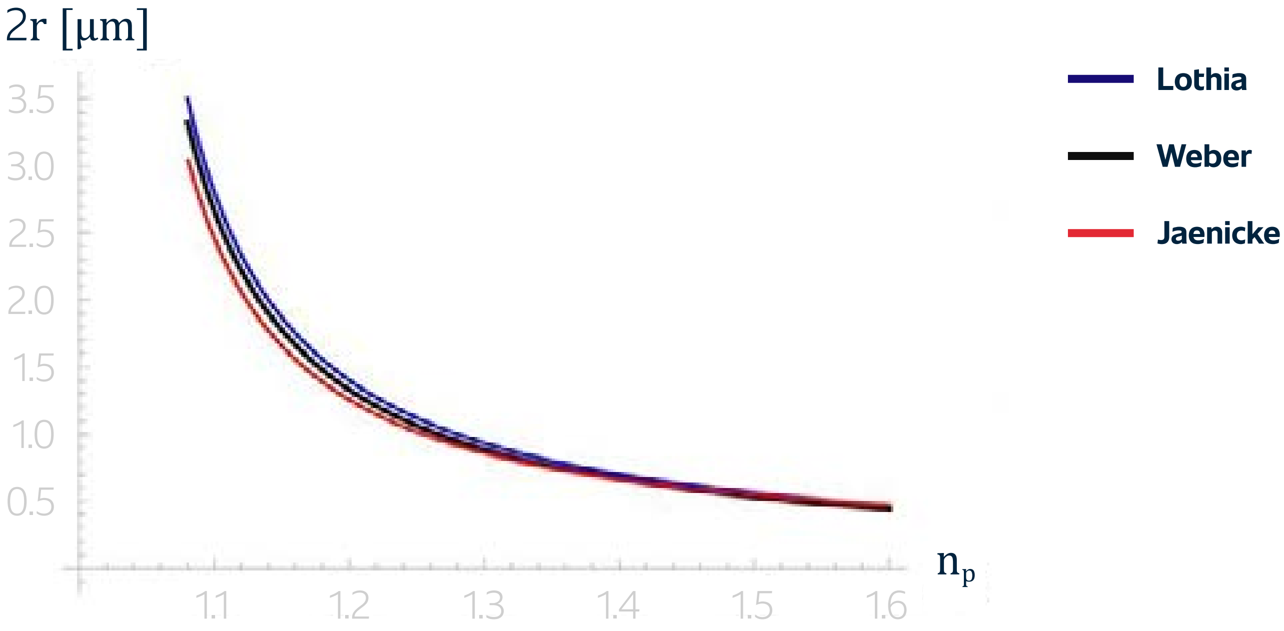

Figure 4: Optimal particle size based on the difference of the particle and matrix refractive indices according to Lothian, Weber and Jaenicke for n_b = 1.0

With these tools one can design a product with the optimal particle size by producing a product of appropriate particle size suitable for the optical properties of the matrix.

Practical application and defining a solution

Several mineralic and organic insoluble pigments have been used as whitening and opacifying substances. Some of them are only permitted in a very limited number of applications, are useable only for very specific applications, are chemically synthesized, or lack the necessary stability for widespread use. In Figure 5 the scattering efficiencies of most common pigments in various matrices are plotted and compared to the whitening and opacifying power of titanium dioxide, which is set arbitrarily to one to allow for an easy comparison.

Comparing the whitening ability of starch, calcium sulfate, tricalcium phosphate, calcium carbonate and magnesium carbonate on a products surface, where the optical contrast is the highest possible, all pigments need to be dosed between 3–4 times the volume amount of titanium dioxide to produce the same theoretical scattering efficiency (blue circles). The scattering efficiency dependency on the refractive index of these pigments is relatively small and the curve has only a minor slope.

If the optical density of the matrix, however, is significantly increased, as in the case for a hard-boiled candy (orange triangles), then the small differences in refractive indices of the pigments have a substantial effect on the ability to scatter light. In this example starch is not an option, excluding for the time being processing limitations, since 50–times the amount of starch would need to be added to produce the same effect as titanium dioxide. Since titanium dioxide is used in such products up to levels of 2% the entire confectionery product would need to be composed of starch. On the other side starch is a good whitener for surface applications.

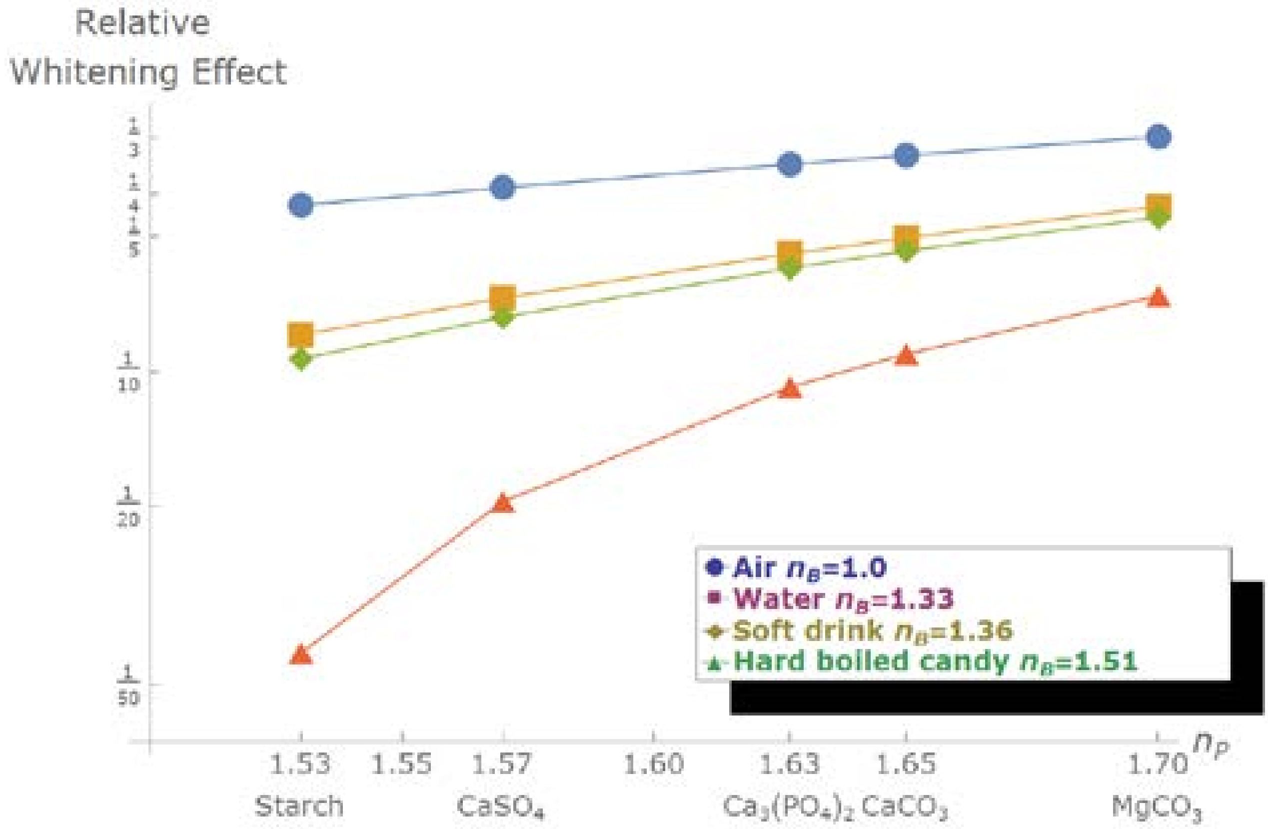

Figure 5: Relative whitening effect of various pigments compared with titanium dioxide (= 1)

In water (yellow rectangles) and in a 10° Bx solution the dosage needs to become more pronounced than for the products in air, but less than in a high refracting sugar confectionery product.

In a typical pet food meat matrix the whitening effect of White Diamond™ is shown in Figure 6. The high refractive index and the strong base material colouring are brightened by the addition of 5% White Diamond™ (d_{50} = 1.6 µm). The observed whitening effect is in line with the theoretical predictions and only marginally different from the calculated whitening effect when compared to titanium dioxide.

In Table 1 the optimal particle size according to Weber is shown for titanium dioxide and White Diamond™, a specific form of insoluble anhydrous calcium sulfate. The optimal particle size of titanium dioxide for the whole range of low and high optical contrast matrices is calculated to be within 0.2 and 0.3 µm. And this is exactly the average particle size range of today's commercially offered titanium dioxide grades. These optimal values are independent from the type of titanium dioxide, rutile or anatase, which differ slightly in refractive index. One disadvantage of such a small particle size requirement is the fact that a certain proportion of commercially available products will necessarily fall within the nano size range (< 0.1 µm), which is an unavoidable consequence of the standard deviation of the particle size distribution.

White Diamond™, due to its lower refractive index compared with titanium dioxide, requires a significantly larger particle size to provide an optimized scattering efficiency, whitening and opacifying effect. Furthermore, there is a strong particle size dependency in relation to the optical density of the matrix, which requires careful selection of the correct particle size to achieve the highest scattering efficiency and in consequence the lowest dosage requirements and cost in use.

Optimal Particle Size and Relative Scattering Efficiency

Product	**Matrix**	**Optimal Particle Size**	**Relative Scattering Efficiency***
TiO2	Surface applications	0.18 µm	1
	Sauce, gels, and wet products	0.23 µm	1
	Extruded and dry products	0.27 µm	1
White Diamond™	Surface applications	0.5 µm	1/4
	Sauce, gels, and wet products	1.3 µm	1/8
	Extruded and dry products	4.6 µm	1/20

*Scattering efficiency of titanium dioxide is set arbitrarily to 1, independent of the application to allow an easy comparison

Table 1: Comparison of the optimal particle size and scattering efficiency of titanium dioxide and White Diamond™.

Comparison of various possible whitening pigments

In Table 2 six dimensions of possible alternatives to titanium dioxide are compared, assessed and rated. Titanium dioxide from a technological and cost-in-use perspective is certainly the best whitening pigment, however the growing public rejection and safety doubts necessitate the removal of this additive from food and feed products. Rice starch and other bleached starches have been used in surface applications where the temperature and moisture sensitivity are not relevant. These applications are however scarce and only relevant for dry applications.

The other mineral pigments can be classified according to their naturalness, their stability and their applicability. Carbonates theoretically have the highest scattering ability, due to their relatively high refractive index compared with the other pigments. The pH instability limits their use, however, to pH neutral applications.

Tricalcium phosphate is synthetically produced and does not fulfill the consumer demand for more naturalness. Talc has the lowest refractive index of all evaluated mineral pigments and therefore has the lowest ability to scatter light. Its use is therefore limited as a separating agent to prevent stickiness of products like chewing gum pieces.

White Diamond™, which is a specific grade of highly refracting, insoluble calcium sulfate seem the best compromise, both from an application as well as from a regulatory and cost in use point of view. The product is obtained by mining from a high-quality calcium sulfate occurrence. Processing is only done by physical treatments, like grinding, drying and milling to the appropriate particle size, to achieve a product with the highest possible scattering efficiency, whitening and opacifying properties.

Product	Naturalness	Applicability	Stability	Cost in Use	Public Perception	Regulatory Status	Overall Average Rating
White Diamond™	**8** As found in nature, dried and milled	**8** Applicable in a wide variety of matrices	**8** pH ad temperature stable	**8** Highly effective due to optimized particle size	**8** Natural and Ca++ supplement	**10** Globally approved as INS 516	**8.3**
Rice Starch	**10** Foodstuff	**2** Only in surface application	**4** Only in low heat and low moisture	**1** High dosage need makes it expensive	**8** Well known and accepted food stuff	**10** Globally accepted food	**5.8**
CaCO3	**4** Additive grade products are synthetically produced	**4** Only in neutral pH applications feasible	**4** pH sensitive	**8** Highly available (paper pigment)	**5** Not well known by the consumer, Ca++ supplement	**10** Globally approved as INS 170	**5.2**
TiO2	**0** Chemically synthesized from Ilmenite	**10** Applicable in a wide variety of matrices	**10** Stable at all processing conditions	**10** Inexpensive, due to low dosage requirements	**0** Growing resistance due to nano particle problematic	**2** Growing global skepticism on the safety (EFSA opinion)	**5.3**
Talc	**8** As found in nature, dried and milled	**2** Very limited to surface applications	**8** Stable at most processing conditions	**8** Inexpensive, but low whitening effect	**1** Not well known by the consumer	**2** Limited use	**4.8**
Ca2(PO4)3	**0** Synthetically produced	**8** Applicable in a wide variety of matrices	**8** Stable at most processing conditions	**4** Expensive due to synthetic process	**5** Not well known by the consumer	**3** Limited use, approved as INS 341(iii)	**4.7**
MgCO3	**0** Synthetically produced	**2** Only in neutral pH applications feasible	**2** pH sensitive	**4** Expensive due to synthetic process	**5** Not well known by the consumer	**8** Limited use, approved as INS 504	**3.5**

Table 2: Assessment and comparison of various whitening pigments

Conclusion

Replacement of titanium dioxide as a whitening and opacifying product for the food and pet food industry just has begun. Several options are available, each of them with specific properties that limits their use. The best compromise in terms of applicability, regulatory status and cost in use is the insoluble form of anhydrous calcium sulfate, which overcomes the stability issues of carbonates and starches.

About Döhler

Döhler (www.doehler.com) is a global producer, marketer and provider of technology-driven natural ingredients, ingredient systems and integrated solutions for the food and beverage industry. Döhler's integrated approach and the broad product portfolio are the optimal basis for innovative and safe food & beverage applications. The product portfolio of natural ingredients ranges from natural flavours, natural colours, health ingredients, pulses & cereal ingredients, dairy & plant-based ingredients, fermented ingredients, dry fruit & vegetable ingredients, fruit & vegetable ingredients to ingredient systems.

Headquartered in Darmstadt, Germany, Döhler is active in over 130 countries and has more than 40 production sites, as well as sales offices and application centres on every continent. More than 7,000 dedicated employees provide our customers with fully integrated food & beverage solutions from concept to realisation.

"WE BRING IDEAS TO LIFE." briefly describes Döhler's holistic, strategic and entrepreneurial approach to innovation. This comprises market intelligence, trend monitoring, the development of innovative products and product applications, advice on food safety and microbiology, food law as well as Sensory & Consumer Science.

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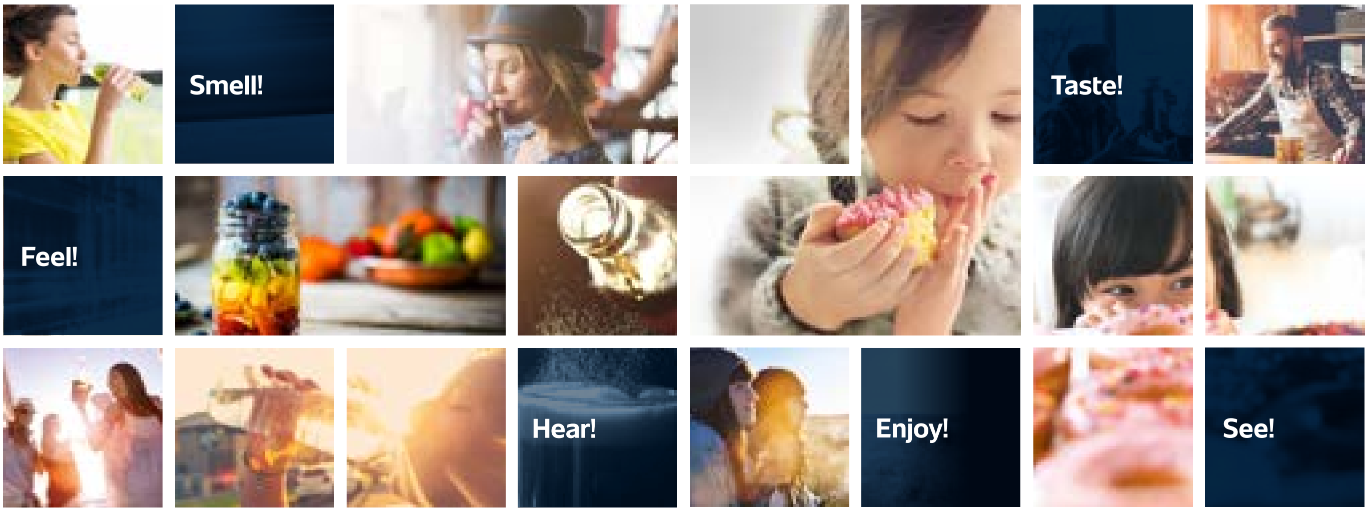

In every innovative product development and product application, Döhler's main focus is always on the multi-sensory product experience, based on appealing harmoniously to all the senses. Thanks to this holistic sensory approach, Döhler is able to guarantee its customers an important building block to success – helping them to stand out from the crowd. Thanks to a diverse product portfolio, Döhler delivers natural ingredients and tailored ingredient systems which are specifically adjusted to every product application and create a perfect multi-sensory product experience.

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