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White Science – A pragmatic solution for replacing Titanium Dioxide

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What is the market need?
Titanium dioxide, TiO_2 (E171) needs to be replaced, since its public acceptance as a food additive has steadily declined in recent years and its technological necessity as a whitening pigment in food is being challenged by consumer groups.
What are the reasons for this?
The naturalness of titanium dioxide is being challenged due to the synthetic chemical process used for producing a white pigment out of a black mineral (ilmenite). Furthermore, questions on the nano scale proportion in food grade E171 are being raised and there are growing consumer reservations about introducing a completely insoluble, inorganic, synthetically-produced molecule into the food chain.
Why has titanium dioxide been used as food additive?
The unique whitening power and the chemical inertness of TiO_2 made it an unchallenged whitening pigment, not only used in the food industry, but also in papermaking, paints, plaster and plastic processing.
What makes TiO_2 unique as a whitening pigment?
The unusually high refractive index, the small particle size and the almost matrix-independent whitening power.

What are the market requirements for an alternative to TiO_2
• Whitening effect in a wide range of food matrices
• Temperature, pH, storage stability
• Inertness towards other ingredients such a vitamins, flavours or colours
• No unwanted sensory impact
• Acceptable cost in use
• Recognised naturalness of the product and manufacturing process

A scientific solution to the problem

The appearance of white is an optical phenomenon based on the reflection of light, which was discovered more than 200 years ago by Augustin Jean Fresnel, and also the scattering of light which was brilliantly described more than 100 years ago by Gustav Mie, linking the so-called size parameter and the relative refractive index of a particle in a given matrix to the scattering cross section. About 50 years later, when computers became capable of calculating the results of Mie's equations, Weber transformed the basic equation, deriving an easily calculable formula relating the optimal particle diameter of the maximal scattering power to the refractive indices of the whitening pigment and the matrix in which the pigment is dispersed. In Figure 1 the optimal particle sizes of several whitening products, which are in principle food grade materials, are plotted in relation to the optical properties of the matrix. Titanium dioxide shows almost no matrix-dependent variation of the optimal particle size, whereas all other whitening products, i.e. magnesium carbonate, calcium carbonate, calcium sulphate, starch or beverage cloud emulsions show a substantial matrix effect. The smaller the optical contrast, i.e. the smaller the difference of the refractive indices of the whitening agent and the matrix (*n_D and n_B*), the larger the optimal particle size becomes.

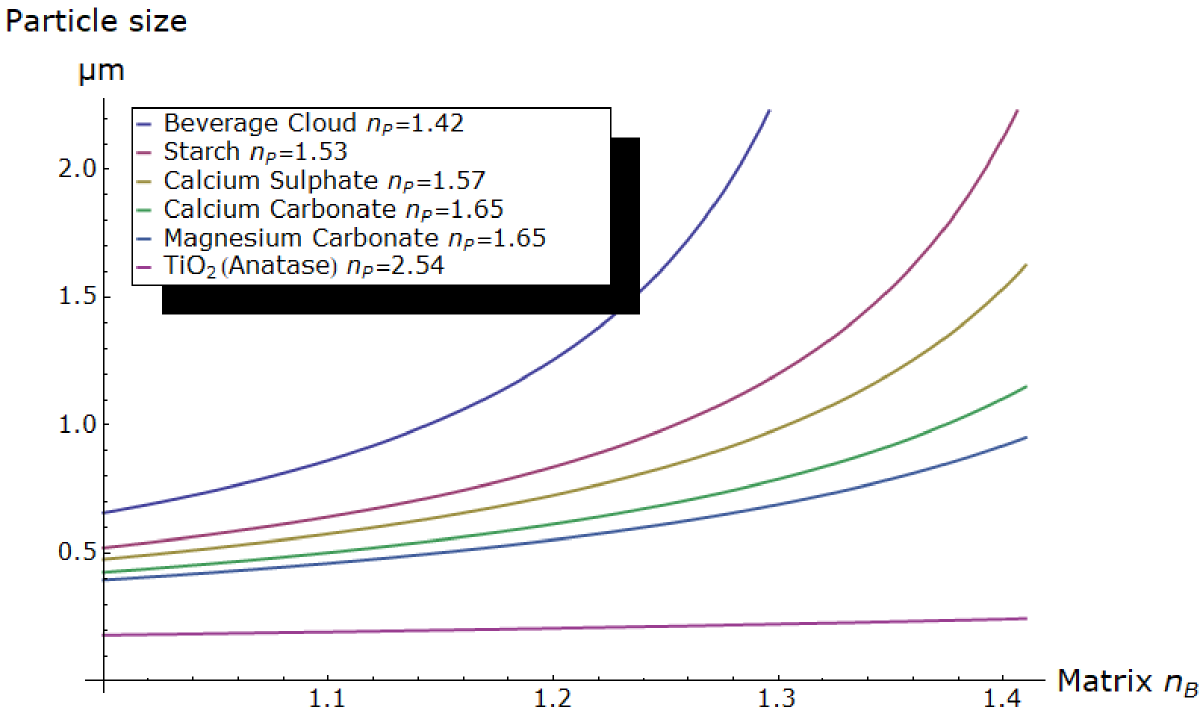

Figure 1: Optimal particle sizes for a maximum scattering power at constant light wavelength according to Weber

What are the practical consequences of these theoretical considerations on technological property requirements of whitening pigments?

In Figure 2 the relative whitening effect of the optimal particle sizes of 4 of these products and tricalcium phosphate is plotted in different matrices and compared to TiO_2 which is set for better comparison arbitrarily at 1. A whitening product which shows its whitening effect on a surface exposed to air, such as in pan coating or whitening a powder blend, can be achieved by almost any material with a refractive index ranging from starch (n_P=1.52) to magnesium carbonate (n_P=1.70), provided the appropriate optimal particle size is used. For applications in aqueous, diet or full sugar beverages the refractive index of the whitening agent already has a more pronounced effect because the optical contrast in the beverage medium becomes smaller. In hard boiled candies, which have a matrix refractive index close to that of starch, starch would need to be dosed more than 50 times compared to TiO_2 to achieve a comparable whitening effect, provided a product with the optimal particle size of about 15 µm is used. The dosage is not realistic, and the particle size of 15 µm would be unacceptable due to the negative sensory effect. On the other hand, starch has been used for panning because the theoretical dosage required is only 4.5 times that of TiO_2 at an optimal particle size 0.5µm. Rice starch, one of the smallest commercially available starches, has a particle range of 3-8 µm, peaking around 5 µm which is almost a magnitude larger than the optimal particle size for whitening with a carbohydrate, resulting only in about 1/5th of the maximum whitening effect. Thus, 20 to 25 times of rice starch is required in panning to yield a comparable whitening effect to TiO_2. This dosage was found acceptable by some producers because the resulting much thicker white layer is usually covered by a coloured coating and the thickness of the white layer is not seen, nor does the sensory effect of the small grain size of rice starch have a significant impact on this particular application and eating habits.

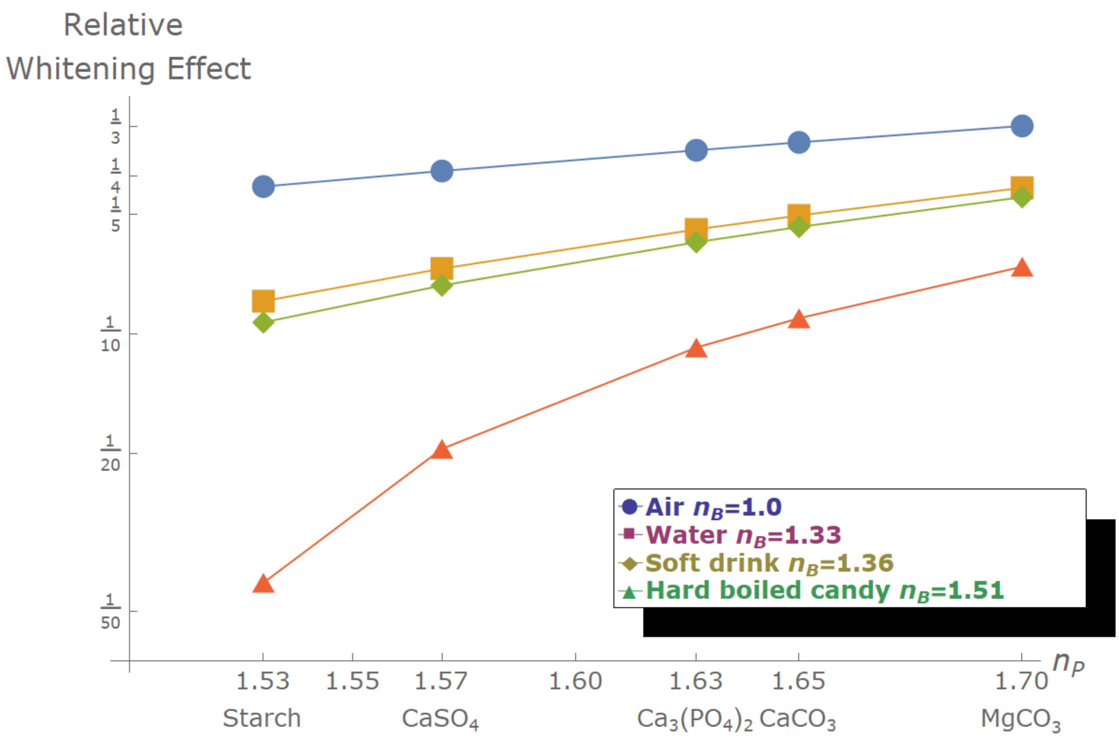

Figure 2: Logarithmic plot of the relative whitening effect of various whitening products

Starch has a very limited application reach besides panning, magnesium carbonate has diuretic side effects, and tricalcium phosphate is synthetically produced and therefore does not meet the consumer's demand for naturalness.

Calcium sulphate and carbonate thus remain as the most promising candidates for replacing TiO2. In Table 1 the dosage requirements of commercially available food grade materials are compared. Even though calcium sulphate has a lower refractive index it outperforms calcium carbonate for two main reasons, i.e. the larger particle size range available which is largely in line with the optimal particle size for whiteness, and the acid stability which allows its use in all food and beverage categories.

Particle size and whitening effect					
Product	Food matrix	Optimal Particle size	Recalibrated* whitening effect	Typical particle size of commercial products	Recalibrated* whitening effect for commercially available products
TiO_2 (n_P=2.54)	Pan coating	0.18 µm	1	0.2 - 0.3 µm	1
	Beverage	0.23 µm	1		1
	Hard boiled candy	0.27 µm	1		1

Calcium carbonate (n_P=1.65)	Pan coating	0.4 µm	3x	2 - 10 µm (d_{50} = 5 µm)	30x
	Beverage	1.0 µm	6x		45x
	Hard boiled candy	2.0 µm	10x		40x
Calcium sulphate (n_P=1.57)	Pan coating	0.5 µm	4x	1 - 4 µm (d_{50}=1.1 µm and d_{50}=4 µm)	12x
	Beverage	1.3 µm	8x		10x
	Hard boiled candy	4.6 µm	25x		25x

*recalibrated to the same whitening effect relative to TiO2

Table 1: comparison of the dosage requirements of calcium sulphate and carbonate with TiO_2

How does calcium sulphate meet the market and consumer expectations?

Calcium sulphate is a naturally occurring mineral which is only processed via physical means. It is poorly soluble in water, but sufficiently soluble to dissolve in the digestive tract to serve in addition as a source for calcium. Its particle size requirement for whitening is large enough to unequivocally put calcium sulphate outside the nano legislation range and need for novel food registration. Sensory impact of calcium sulphate is negligible, which is in contrast to calcium carbonate.

Cost in use for calcium sulphate is the lowest of all evaluated TiO_2 alternatives so far, due to its lower practical dosage requirements for achieving the same whiteness and its basic cost structure. Döhler has pioneered and patented the development of calcium sulphate as a whitening product in many food and dry beverage applications, and it is an approved additive and supplement in all major regulatory regions like EFSA, FDA or JECFA.

Integrated Natural Colour Solutions

Doehler's colouring solutions are based on pure natural products, with the colours being extracted from fruits, cereals, vegetables, malt or other plant-based raw materials. Vegetables are particularly well suited as a raw material in the production of natural colours because they remain stable despite light, heat and other chemical and physical influences.

As a provider of complete ingredient systems and integrated solutions, Doehler's primary focus is on the development of innovative concepts. In line with the company slogan “We bring ideas to life.”, Doehler develops custom complete solutions, processes and innovations for its customers – from the field to the supermarket shelves.

About Doehler:

Doehler (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. Doehler'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, Doehler 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 Doehler'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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