Innovation Spotlight
TONSIL®

CLARIANT

Mineral refinement

Issue: **Spring 2014**

Tonsil® – efficient purification of edible oils based on natural resources

What has a volcanic eruption to do with a juicy roast steak? The connection between volcanic ash and the golden yellow edible oil in the kitchen – widely used for roasting, deep frying or for salads – is not immediately apparent. What they have in common is the purifying effect of so-called bleaching earths based on the natural resource bentonite, one of these clay minerals which were able to form over the millennia under certain pressure and temperature conditions from deposits of volcanic ash in subterranean deposits. It is used to produce the highly active bleaching earth Tonsil® which gently removes all undesired accompanying substances and dyestuffs as well as impurities from edible oil whilst preserving the nutrients, thereby creating ideal preconditions for healthy consumption and a clear appearance.

Worldwide, about 157 million tons of edible oil are extracted every year from the seeds and fruit of oil-rich plants, with mainly rapeseed oil being produced in Europe and Canada, palm oil in Asia and sunflower oil in Eastern Europe. In North and South America, on the other hand, soybean oil is favored. The oil content of the oil seeds and fruits used varies: in relation to its dry weight, rapeseed contains an average of about 40 percent oil, while the fruits of the oil palm and sunflower seeds have the highest oil content with just under 50 percent. Last in the ranking come soybeans with an oil content of only about 20 percent. Regardless of what plant the edible oil is sourced from, to give it a long storage life and make it heat resistant as well as neutral in taste and odor, it is not just pressed and filled in a container – it first has to be purified to remove undesired substances. Bleaching earths derived from the natural resource bentonite play a central role in this refining process.

CLARIANT PRODUKTE
(DEUTSCHLAND) GMBH
BUSINESS LINE ADSORBENTS
Ostenrieder Straße 15
85368 Moosburg
Germany

WWW.CLARIANT.COM
WWW.INNOVATION.CLARIANT.COM
WWW.FUNCTIONALMATERIALS.CLARIANT.COM

From mineral to bleaching earth

Large deposits of bentonite are present, for example, in the Moosburg area of Bavaria, Germany. The mineral has been surface mined here since 1906. These deposits are estimated to last for at least the next 30 years. Clariant leases the land on which the valuable raw material is mined from the farmers, and renatures it afterwards to their specifications. Although this increases the cost price of the raw material, this is compensated by low transport costs. Clariant is therefore fully living up to its responsibility for ensuring sustainability.

Bentonite is a mixture of different clay minerals. Besides various accompanying minerals, such as quartz, mica, feldspar or calcite, its most important constituent is the mineral montmorillonite (60 to 80 percent) – a so-called layered silicate (aluminum hydrosilicate). It consists of several layers or lamellae of silicon and metals such as aluminum and iron, as well as calcium and magnesium ions intercalated between the layers. Thanks to this special structure and the ions intercalated within it, it has an enormous water absorbency and a high ion exchange capacity – making it ideal for use as the highly active bleaching earth Tonsil® for purification of edible oils. The nature of the raw material is decisive for the later performance characteristics of the bleaching earth.

The Clariant product Tonsil® is formed by a so-called acidic activation of the raw material bentonite. The aim of this process is to activate the binding sites and enlarge the surface of the raw material. This is achieved by adding a mineral acid to a finely milled and heated bentonite suspension. The protons (H^+) of the acid attack the individual lamellae from all sides and replace the interlayer cations (calcium and magnesium ions). A large proportion of the metals (aluminum and iron ions) within the lamellae are also released by the protons. The binding sites of the clay mineral are now activated and ready to absorb other substances. The layered structure of the bentonite changes greatly during the activation process: the ion exchange with the protons enables additional water to enter between the layers and the mineral swells. The surface area thereby increases fivefold to about 300 m^2/g. The final degree of activation of the bleaching earth can be precisely controlled by adjusting the acid concentration, the temperature and the exposure time. In the purification process, all undesired accompanying substances and impurities from the oil can be bound to the now activated and greatly enlarged surface.

The metal ions released in the activation process are a valuable by-product: they are separated and used for phosphate precipitation in wastewater treatment plants. Phosphates entering wastewater adversely affect the nutrient balance in waters and in the soil. With the aid of precipitating agents such as aluminum or iron salt, they are converted into a solid allowing them to be easily removed from the wastewater.

THE CLAY MINERAL BENTONITE
is mined in open pit mines.

Tonsil® makes edible oil storable and flavorful

Washed, dried and milled to the optimal grain size, the bleaching earth Tonsil® is ready for use in edible oil purification. Beforehand, however, the phosphatides are removed in a first step known as degumming. The mechanical force exerted by the press breaks open the cell membranes of the oil fruits consisting of two layers of phosphatides. Fragments of these membranes enter the oil, where they would adversely affect the taste, clear appearance and shelf-life. To break down these gums and separate them from the oil citric acid and a certain amount of water are added.

Not only gums, but also dyestuffs and peroxides – strong oxidizing agents produced by oxygen attacking the double bonds of unsaturated fatty acids – and even heavy metals and residues of crop protection agents may be present. All these substances can be removed from the oil by means of the bleaching earth. The milled Tonsil® is added to the untreated oil in a dosage of about 1 percent of the total amount. Under vacuum and at about 100 °C, the Tonsil® particles are stirred until evenly distributed. Large molecules of the dyestuffs like carotinoids and chlorophylls as well as crop protectant residues are adsorbed in the interior of the Tonsil® particles. Here, the positively charged heavy metal particles displace the protons and are bound to the Tonsil® in exchange. The catalytic decomposition of peroxides also takes place in the outer layer of the highly active bleaching earth. The Tonsil® binding sites occupied by protons are capable of attacking the oxidation promoting functional groups of the peroxides and eliminating them while separating off water. Further oxidation, which would make the oil quickly turn rancid, is thereby prevented. After the reaction, the Tonsil® particles are filtered out through presses.

Finally, deodorization is performed. In this steam distillation process, remaining free fatty acids and aldehydes are removed under vacuum to stabilize the shelf-life and taste. No waste is produced throughout the entire process. The free fatty acids and aldehydes are used as basic chemicals in industry. With its high calorific value, the spent Tonsil® accounting for 30 to 35 percent of oil residues – similar to the energy reserves of lignite – is for example very useful in cement production or as a valuable raw material for energy production in biogas plants.

Clariant is the world market leader in the purification of edible oils. More than one third of the world's annual production of oils and fats is purified with Tonsil®. Using natural resources, Clariant thereby makes an important contribution to healthy nutrition – in harmony with nature.

Chemistry **EXPLAINED**

ANIMATION WITH SOUND AVAILABLE AT:
WWW.INNOVATION.CLARIANT.COM

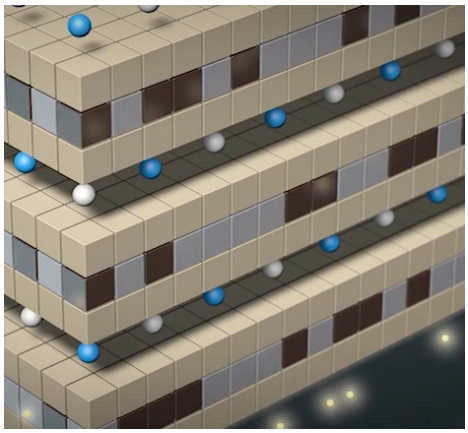
Crystal structure and ion exchange reaction

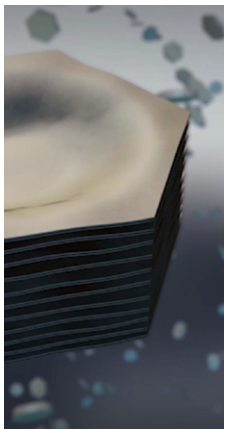
The elements of clay minerals are arranged in so-called crystal lattices. These are highly organized structures in which all the components involved are arranged at regular intervals in the three-dimensional space. Their constellation is based on the lattice forces, specific forces of attraction and repulsion through which the individual elements interact with and maintain their distance from each other, e.g. ionic or covalent binding forces.

A single montmorillonite crystal of bentonite consists of three superimposed layers with interlayer spaces between them. The layers are not rigidly connected to each other, but swell when water and other substances enter between them. The two outer lamellae consist mainly of silicate (SiO_4^{4-}). They enclose a middle layer with a high content of aluminum ions (Al^{3+}). Overall, the layers are negatively charged, a situation compensated by cations, positively charged ions, intercalated in the interlayer spaces. These loosely bound cations are mobile within the interlayer spaces and can easily be replaced by other ions of higher binding affinity. This is the necessary precondition for the clay mineral to function as an ion exchanger.

Ion exchangers in general are materials capable of exchanging part of the ions bound to them for the ions of the solution surrounding them. A distinction is made between cation exchangers (exchange of positively charged particles) and anion exchangers (exchange of negatively charged particles).

The acidic activation of bentonite with the aim of producing the highly active bleaching earth Tonsil® is based essentially on an ion exchange reaction of this kind in the crystal lattice. An excess of protons is generated by adding a mineral acid. The interlayer cations, in other words the positively charged particles, are replaced by these protons and the metals inside the lamellae are partly mobilized and released. The binding sites of the bentonite are now activated, and more water molecules can enter between the layers – the clay mineral swells. When the excess acid has been removed from the activated bentonite, other substances can now easily attach themselves to the binding sites of the enlarged surface.





SCHEMATIC REPRESENTATION of the layered crystalline structure of the bentonite. Magnesium and calcium ions are intercalated between the layers.

CRUDE BENTONITE ENLARGES ITS SURFACE fivefold after activation with mineral acid.