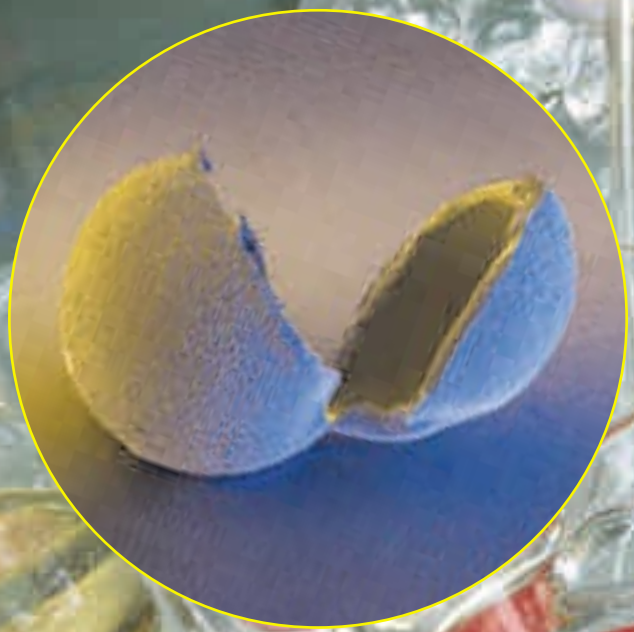
Microcapsules give textiles a delicate fragrance

The world's tiniest perfume bottles

Leather car seats redolent of the Caribbean? No problem with microcapsules made of plastic. Research scientists at Bayer Chemicals have developed a new technology for "packaging" fragrances in an ultra-thin nanofilm to form microcapsules. Leather and textiles sprayed with these microcapsules then release a soothing or exotic fragrance, depending on the particular perfume used, when subjected to pressure.



Doris Gansen tests the waterproofness of leather samples which will later be sprayed with microcapsules. (Small photo: A ruptured capsule as seen through an electron microscope.)

Dr. Martin Kleban with high-quality furniture upholstery leathers which can now be treated to exude a pleasant fragrance.

Transparent balls, tightly packed, all higgledy-piggledy, shimmering and sparkling, seemingly floating. Are they soap bubbles? Marbles? No, they are in fact microcapsules made of plastic that are too small to be seen with the naked eye. Each individual microcapsule is actually only about five micrometers in diameter – in other words no more than a few thousandths of a millimeter. And their special characteristics can also only be seen under the microscope: their shells are extremely fine, yet more stable than soap bubbles, transparent and highly elastic. The film surrounding the capsules is just a few nanometers thick and is made of the plastic polyurea. It's hard to imagine that such minute capsules can be filled with anything. Yet they contain tiny quantities of perfume. When the nanofilm is subjected to pressure, it bursts like a balloon and releases its fragrant content. For example, when a car driver leans back in his leather seat, he is surrounded by the fresh fragrance of "Blue line".

"Blue line" is one of two fragrances that the leather specialists at Bayer Chemicals, a division of Bayer AG, have packaged into microcapsules which are finely dispersed in a liquid and then simply sprayed onto the leather. The other, called "Cuir naturelle vitessence", imparts that familiar scent of genuine leather that modern leather products lack. These two fragrances are the first in the Euderm® Aroma range of products developed by research scientists at Bayer Chemicals for the leather processing industry. Others are to follow. For microcapsules are the ideal packaging for all sorts of fragrances. "For example, you could have sports shoes with a citrus fragrance, leather armchairs that exude a soothing or stimulating aroma, or designer products containing microcapsules with an appropriate perfume," says Dr. Martin Kleban, a specialist in leather finishing products in the Research and Development Department of Bayer Chemicals' Leather Business Unit.

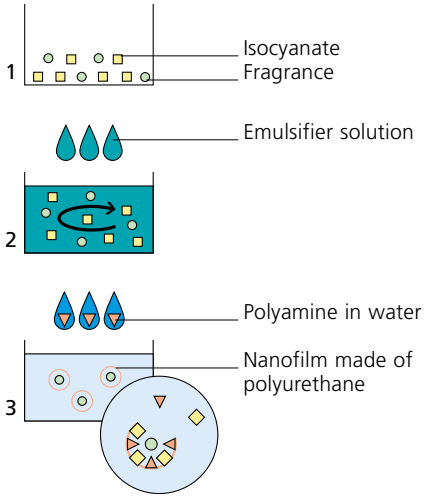
Millions of fragrance capsules are trapped between the fibers

The individual fragrance capsules cannot be seen in the milky white liquid which is sprayed onto the leather product, nor is there initially any trace of perfume. This is due to the nature of the microcapsules, which are so tiny that the mixture is easy to process, yet prevent the perfume from evaporating before it is actually needed. The product is easy to apply, as Kleban explains: "Simply spray it on, leave it to dry for a minute and you have leather with a long-lasting fragrance." Millions of the microscopic phials of perfume are trapped between the fibers – some deep down, others nearer the surface. As long as the sports shoes or armchair are stored in the warehouse, the fragrance remains encapsulated in the leather. It is only when they are used that they gradually release their content. Whenever anyone sits down to relax in the armchair, for example, some of the capsules rupture and envelop the occupant with their sweet-smelling fragrance. And this release-on-demand principle, as it is known, is not only suitable for perfumes.

The hollow capsules can be filled with other substances as well, provided they are liquid or dissolve in special auxiliaries, but not in water – dyestuffs, for example. It was with dyestuffs that Bayer first ventured into microencapsulation technology in the 1970s. At that time, some researchers in the company were working on the basic

Why leather no longer smells like leather

It used to be the case that if you wanted to know whether a jacket, a new wallet or a pair of boots was made of genuine leather and not some cheap imitation, all you had to do was smell it. The characteristic smell of real leather derived from the various products used in processing the animal hides. In the olden days, tanners treated the raw hides with oak bark and other woods, and then they used fish oils to make the leather more supple. These and other components were what gave leather its unmistakable odor. Nowadays it is impossible to tell whether it is the real thing or not. Tree bark and fish oil have largely been replaced by synthetic tanning materials and finishing agents, leaving leather with only a very slight inherent odor.



How the fragrance gets into the capsule
The fragrance and the water-insoluble polyurethane component – the isocyanate – are mixed **1**. A mixer then disperses the fragrance/isocyanate mixture in the emulsifier solution as very fine droplets of the desired capsule size **2**. The second polyurethane component, the polyamine, is then added in aqueous solution **3**. This triggers the actual encapsulation process. The two polyurethane components react by means of interfacial polymerization on the surface of the micro-droplet to form a solid nanofilm of polyurethane containing the fragrance. The finely dispersed microcapsules float in the dispersion, which is then ready for spraying onto the relevant product.

Dr. Nils Brinkmann prepares a new mixture for the production of fragrant microcapsules.

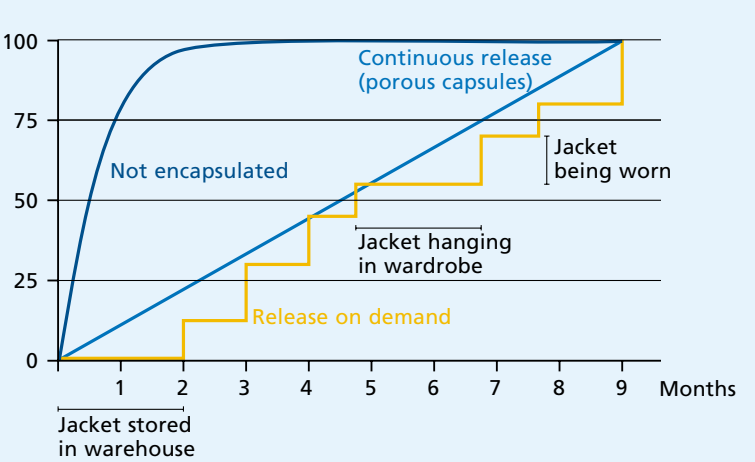
Microcapsules have also proven effective as a delivery form for certain active ingredients used in crop protection products. In the first place, the nanofilm protects the farmer, as it prevents him from coming into contact with the active ingredient when handling the product. And, as in the case of perfumes, it prevents the active ingredient from evaporating prematurely. However, as the principle of release through pressure is not applicable with crop protection products, the capsule shell for these is covered in tiny holes. Dr. Hilmar Wolf, a scientist in the Formulating Technology Department at

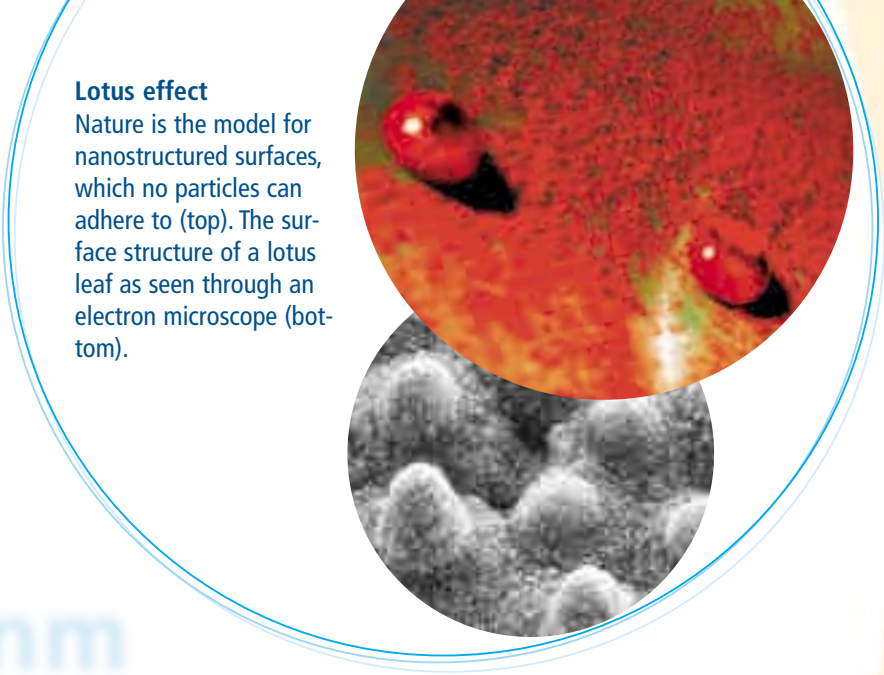
principles of a technology for the carbonless coating of copying paper. They enclosed the dyestuff in microcapsules, which were then applied in a thin layer on the back of the paper. The advantage of this is that you don't get your fingers dirty when handling the paper, but when pressure is applied by a ballpoint pen, the dyestuff is released in the form of visible markings. Bayer is still a leading licensor of this technology.

However, it was only when the microcapsules were reduced even further in size that new possibilities were opened up. Today, the microcapsules range in size from a few hundred nanometers to one millimeter. Five micrometers is ideal for treating leather. Explains Kleban: "The capsules have to be small enough to penetrate into the leather, but at the same time large enough to be trapped between the fibers."

Long-lasting scent

If not encapsulated, fragrances evaporate within a few weeks. Capsules with a porous shell release their content steadily over many months. If the capsule wall is rigid, it only releases the fragrance if it is ruptured (release-on-demand principle). As only a few of the capsules burst at any one time, the effect lasts for months.





Lotus effect
Nature is the model for nanostructured surfaces, which no particles can adhere to (top). The surface structure of a lotus leaf as seen through an electron microscope (bottom).

Bayer CropScience, explains one of the advantages of this technology for the crop protection sector: "It guarantees that the active ingredient is released gradually over an extended period." Whether the microcapsules contain a crop protection product, dyestuff or perfume, and whether they have solid or porous walls, the encapsulation technology is always the same: interfacial polymerization. In developing this process, the researchers at Bayer Chemicals made use of the reaction mechanisms involved in the production of polyurea and the properties of the pre-products. The polyurea used for the nanofilms is made up of two components – polyamine and isocyanate. The former is water-soluble, whereas the latter is not. When the two pre-products come into contact, they react with each other to form a solid, but elastic plastic.

Fragrances packaged in a nanofilm made of plastic

Kleban explains what happens when fragrances are encapsulated: "The first step is to mix the perfume with a carrier oil and the water-insoluble plastic component." Then an emulsifier is added, and a dispersing unit like a large mixer disperses the fragrance/isocyanate mixture as very fine droplets of the desired capsule size. Next, an aqueous polyamine solution is added slowly and carefully. Kleban continues: "The isocyanate molecules on the surface of the droplets of oil react with the surrounding polyamines in the water to form the capsule shell and thus enclose the fragrance." Nothing is left to chance – neither the size of the capsules nor the thickness of the nanofilm nor the degree of permeability. The Bayer experts can determine all these parameters through skillful combination of the individual substances and the way in which they are processed. "The size of the capsules depends, for example, on how fast the components are mixed," says Kleban. Another advantage of this technology is that after the encapsulation process, no further operations are required. The dispersion is ready for industrial use.
Sooner or later, of course, the last capsule in the leather bursts. However, Bayer's experts have thought of this, too. "We are currently working on a leather care product with microcapsules that can be used to replenish the desired fragrance," says Kleban.
Having proven successful for leather, the technology is now also being applied to fabrics. Scientists at Bayer Chemicals in Italy have developed a similar microcapsule dispersion known as Bayscent® for incorporating in textiles. Hans-Albert Ehlert, head of Strategic Product Management for textile processing chemicals at Bayer Chemicals, explains one of the few differences: "Bayscent® contains special auxiliaries that bind the microcapsules so strongly to the fiber that they can withstand several gentle hand-washes." Ten fragrances are available so far – all of them, like the leather fragrances, created by Symrise, the successors to Bayer's former subsidiary Haarmann & Reimer. There is virtually no limit to the potential applications: for example, carpets that give off the spicy scent of sandalwood at every step, or pale blue sofas that envelop you with the soothing perfume of lavender when you stretch out after a hard day's work. The range also includes refreshing aromas such as forest fruits and lime. Other capsules are filled with natural essences which promote physical and spiritual well-being.

Christoph Roth sprays a leather sample with a new fragrant mixture.

www.bayerleather.com
Further information on the leather production process can be found under the "Leather Info" button.