Textile Materials with Fixed Cyclodextrins as a Fragrance Depot

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The ability to semi-permanently infuse fabrics with finished fragrances and/or fragrance materials opens up a new realm of formulation and application possibilities for perfumers. The market has already seen the introduction of scented pillows and the like, but Buschmann et al.'s recent work presents the possibility of (washable) scented sportswear, linens, upholstery and many other household products that may be customized at will, and which may intake unpleasant odors while imparting pleasant ones.

Textile materials are ubiquitous in our surroundings. In the private sphere, this primarily includes fabrics for clothing, furniture and other home applications. There is a high consumer demand on the performance of such materials, especially in clothing. Wearable textiles should theoretically impart a positive feeling upon the wearer, particularly in the way it feels against skin.

Working against the positive aspects of fabrics is the fact that they easily adsorb odors and release them slowly.[1,2] Unfortunately, this mainly happens with unpleasant odors. After visiting a pub, for instance, one may notice the smell of cigarette smoke released from his or her clothing. In this same way, curtains, upholstered car seats and other textiles are able to store unpleasant odors for long periods of time. Most commonly, airing or cleaning of these textiles removes "bad" odors. Spraying the material with fragrances can mask "off" odors for some time, but this strategy is ultimately ineffective.

The microbiological decomposition of the organic substances contained in perspiration is responsible for the development of malodor of sweated sportswear or leisurewear. The same process for the formation of body odor takes place in all textiles upon physical contact with flesh; only the amount of odor substances formed is different. To take hide the smell of body odor, many people spray the affected textile with perfumed products before (or after) use, or employ antiperspirants. Because the components of perfumes are volatile, nearly all the fragrances applied to fabrics fade away fairly quickly. This process is accelerated by the body heat.

It is possible to produce long-lasting perfumation of textiles by microencapsulating fragrances. Such microcapsules must be fixed to the textile surface. During the usage of the textile — via the application of pressure (flesh against clothing) and/or heat (body heat/environmental heat)—— the microcapsules are broken, thus releasing the encapsulated perfume. One disadvantage, however, with the microencapsulated perfumes, is that the user of these textiles is not able to choose just any fragrance they desire — that is left up to the producer of such fragrance-carrying clothing. In addition, the release of perfume slowly diminishes as more and more of the microcapsules are broken.

Through our collective research at the Deutschen Textilforschungszentrum Nord-West e.V, we have developed a textile-finishing method. It enables the production of textiles with properties not attainable with other methods.[3] In this new method, the permanent fixation of cyclodextrins to fabric allows the molecules to act as long-term depots for perfumes.

Properties of Cyclodextrins and their Complexes

Cyclodextrins (see Figure 1) are polysaccharides built from six to eight (a=6, ß=7, g=8) D-glucose units, and are formed during the enzymatic degradation of starch.[4] The D-glucose units are covalently linked at the carbon atoms C_1 and C_4. Cyclodextrins were mentioned in literature for the first time more than 100 years ago. At that time, nothing was known about the structure of these molecules. The cavity radii of these relatively rigid molecules vary between 0.50 nm and 0.85 nm. A large number of hydroxyl groups are located on the outside of the molecules. As a result, cyclodextrins are soluble in water. However, the cavities are formed by the non-polar groups of the molecules. Thus, non-polar guest molecules can be housed within them. For the formation of complexes between cyclodextrins and guest molecules, it is not essential that the guest molecules be completely enclosed within the cavities.[4] Due to the complex formation, the physical and chemical properties of the guest molecules are changed. Some changes are important for the application discussed in this article:

Stabilization of guest molecules against:

- heat and light;
- oxidation or hydrolysis;
- evaporation;
- chemical reactions between differently complexed molecules.

Clothing and home textiles often come in contact with human skin. Therefore it is essential that there be no potential health risk for humans. The results of several animal experiments have displayed no acute toxicity, even

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Figure 1. Schematic structure of cyclodextrins (a-CD: n=1, b-CD: n=2; g-CD: n=3) (dimensions in pm)

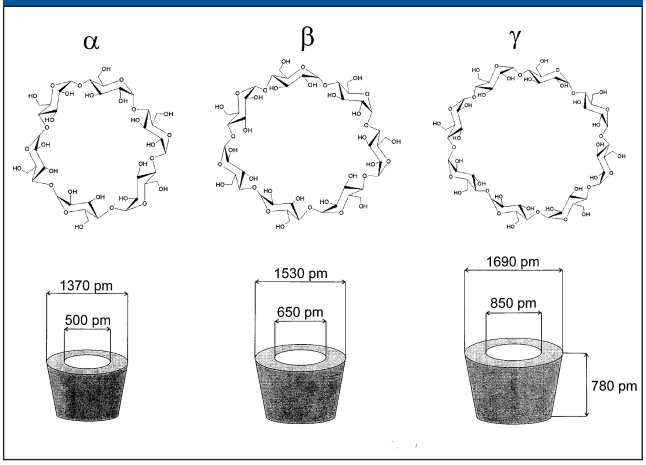
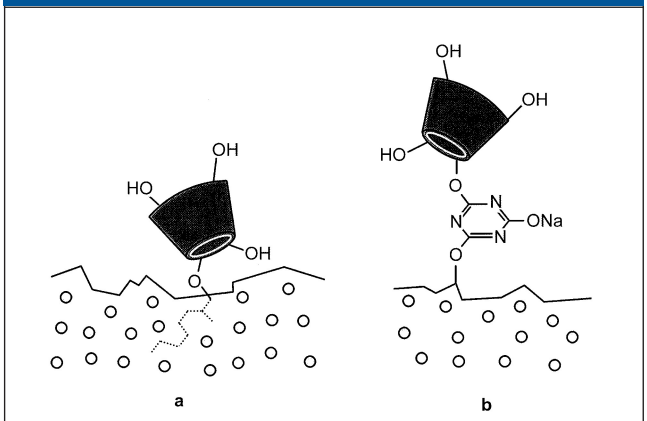


Figure 2. Fixation of cyclodextrin derivatives with hydrophobic (a) or reactive groups (b) on a polymer surface



upon oral administration of high dosages of cyclodextrins.[5] Since November 2000, ß-cyclodextrin has been licensed as a food additive in Germany. In other countries, including Japan and the United States, ß-cyclodextrin has long been used in the food industry. Toxicological data have been reported for the monochlorotriazenyl-substituted b-cyclodextrin derivative.[6] According to OECD tests, this cyclodextrin derivative has no irritating or sensitizing effects. This derivative can be permanently fixed on cellulosic materials, such as cotton. Comparable results for textile materials treated with this cyclodextrin derivative are expected. These expectations are supported by the first clinical trials with textiles in which no irritation of the human skin could be detected.[7]

Permanent Fixation of Cyclodextrins on Textiles

To combine the properties of cyclodextrins with textile materials, it is necessary to bind the cyclodextrin molecules permanently on the fiber surface.[3] In principal, cyclodextrins with suitable substituents can be fixed on the surface of different polymers.[8-10] For example, a reactive anchor group may be used in the case of cellulosic materials, and an alkyl chain for polyester fibers (Figure 2). The fixation process of cyclodextrins can be compared with dyeing of the different textile materials. In Germany the first textiles with cyclodextrins are already offered.

Properties of Textiles with Fixed Cyclodextrins

Cyclodextrin molecules on fabrics may be used as a depot for fragrances placed by fragrance producers, textile manufacturers or in the home by consumers. Wet or dry textiles can be sprayed with fragrance solutions (consumers could also theoretically place some drops of perfume material into a tumble drier). In the treated textiles' dry state, fragrance molecules are complexed by the cyclodextrins, where they may be held for months or, in some cases, even years, due to the reduction of vapor pressure.[11] Even an increase of temperature does not accelerate the evaporation of the fragrance molecules. The complexed molecules are only released in the presence of moisture present near the skin surface. Simultaneously, the organic compounds from sweat can be complexed.

Because the cavities of cyclodextrins can be refilled after washing, each individual may be able to choose his or her own fragrance according to individual taste (perfumes, menthol, lavender, eucalyptus oil and many other substances can be complexed by the fixed cyclodextrins).[12] The complexation of these substances are appropriate for

bed linen or similar home textile applications because the release of fragrances is often associated (by the consumer) with a calming effect.

The fixation of cyclodextrins on clothing can result in some changes in their properties. In the simplest case, the cyclodextrin cavities are empty. Thus, they are able to encapsulate the lipophilic organic components of perspiration, or of the substances formed during the microbial degradation of them.[13] The vapor pressure of these complexed substances is reduced. Because of this, the formation or, respectively, the perception of body odor is suppressed. So, "off" odors may be disposed of while pleasant scents are dispersed.

After all cyclodextrin cavities are filled, these textiles should be washed like any other textiles. During a normal washing process of textile materials treated with cyclodextrins, the complexed organic substances are removed along with any other impurities. However, due to their fixation, the cyclodextrin molecules remain on the textiles, allowing for continued fragrance action.

Acknowledgements

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