应用于建筑领域功能涂料的环糊精香料复合物

Cyclodextrin Fragrance Complexes for Functional Coatings in the Construction Sector

许多香精油和其它香料物质都具有生物效应的广谱特徵——能够改变人的情绪、对抗细菌、击退有害物等。但是，由于这些香料物质同时具有挥发性，会极快地降解，因此到目前为止仍然很少应用于工业产品中。现在，首次开发成功的稳定方法——环糊精分子包合法——使得非憎水涂料和装饰产品使用香料成为了可能。

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提到"香精油"，我们会联想到气味强烈的植物，如茉莉、玫瑰、薰衣草、柠檬皮、香草等。但这些挥发性的物质却不仅仅只是气味好闻而已。近年来，工业界已经日益注重其生物效应。主要集中于三个方面的效应：首先，香味会由于气味感官和边缘系统的紧密偶合而影响人的状态和心情；其次，大多数的芳香气味还起到驱赶动物的作用；第三，一些香味还有显著的抵抗细菌功能，例如能够杀灭或阻止细菌、真菌和酵母菌的增殖。所有这些效应在人类觉察不到香味的浓度下达到。

所以，建筑专家意识到使用香精油及其它物质不足为奇，他们采用许多方法在涂料及饰层材料中开发应用具有生物功能作用的香料物质。在建筑应用中，主要在于使用香料为大面积范围应用的含粘合剂建筑材料增加特别的功能性。

例如，含有驱赶鸟类芳香气味的建筑物外墙涂料或饰层就可以驱赶鸽子，避免建筑物上堆积令人不悦并危害健康的鸟类排泄物。研究表明，橙花油中的氨基苯甲酸甲酯具有驱赶鸟类的作用。内墙涂料可以用于改善室内空气的嗅觉质量并驱赶有害或令人烦恼的虫子如蚊子等。例如，飞蛾一般会避开薰衣草花，蚊子和马蝇会躲避丁子香酚和香叶醇的味道。许多年来，研究机构尤其是热带地区的研究机构一直在寻找利用香精油驱赶蚊子或白蚁等昆虫的方法，作为控制或防止疟疾和黄热病的方法之一。

所有的应用中还可以进一步获得额外或替代性的抗菌功能。许多古老的家居药品和越来越多的化学药剂都已经利用香精油的抗菌功能。例如，一些科学研究已经表明从红百里香中提取的香油具有抵抗细

Many essential oils and other fragrances are characterised by a broad spectrum of biological effects – they can for instance change your mood, combat microbes and repel pests, to name just a few. But they are also volatile and quickly degrade so that industry has barely exploited them at all so far. Now for the first time, a recently developed stabilisation method – molecular inclusion in cyclodextrins – makes it possible to use fragrances in non-hydrophobic coatings and linings.

Mention "essential oils" and we think of strong-smelling plants, of jasmine, rose, lavender blossom, lemon peel or fragrant herbs. But these volatile materials do far more than just smell good. Industry has focused increasingly on the biological effects – as opposed to the odour – of fragrances in recent years. The main focus is on three effects: firstly, fragrances can affect moods and emotions because of the close coupling between the sense of smell and the limbic system. Secondly, a large number of fragrances act as animal deterrents. Thirdly, some fragrances have notable antimicrobial activity, i.e. they either kill or stem the proliferation of bacteria, fungi and yeasts. All these effects can be unleashed at concentrations at which the fragrance is imperceptible to humans.

It is not surprising, then, that construction specialists have also become aware of essential oils and their potentials. Ways are being explored of exploiting this biological action spectrum of fragrances in coatings and linings as well. For construction applications, the main interest lies in using fragrances to add extra functionality to binder-containing construction materials which are applied to large areas.

For example, a coating or lining containing a bird-deterring fragrance on the outside of a building might keep away pigeons and their unappealing and health-threatening droppings – studies proved that the methyl

菌和霉菌的高效功能。因此，可以加入合适的香料以阻止真菌攻击一些特定的物质(饰层、涂料、腻子和密封剂)。

直到目前，这些类型的应用还不是非常可行，主要就是因为香料物质具有较高的挥发性和化学敏感性。涂料中的许多香料物质只要几天就会失去其本身的味道(**图1**)。例如，由于曝露在空气和光线中它们的一些成分会被氧化，还有一些会在热或酸、碱的作用下发生化学变化。这样就使香精油失去效用，在某些极端的情况下还会转变成有害的物质。当加入石膏浆或液体涂料中时，有些香料甚至不能抵抗混合时的分散剪切作用。但是，作为一个补偿，香精油及其组成物还有另外一个优点：就目前所知，微生物还没有对香精油显现出抵抗性。

鉴于这些原因，需要建立一个体系能够在涂层干燥后保护这些敏感物质并且在很长时间范围内使其以受控的方式释放出来。德国瓦克化学品公司 目前已经开发了这种释放体系：该体系是利用分子包合的原理将香料物质包入环糊精中。

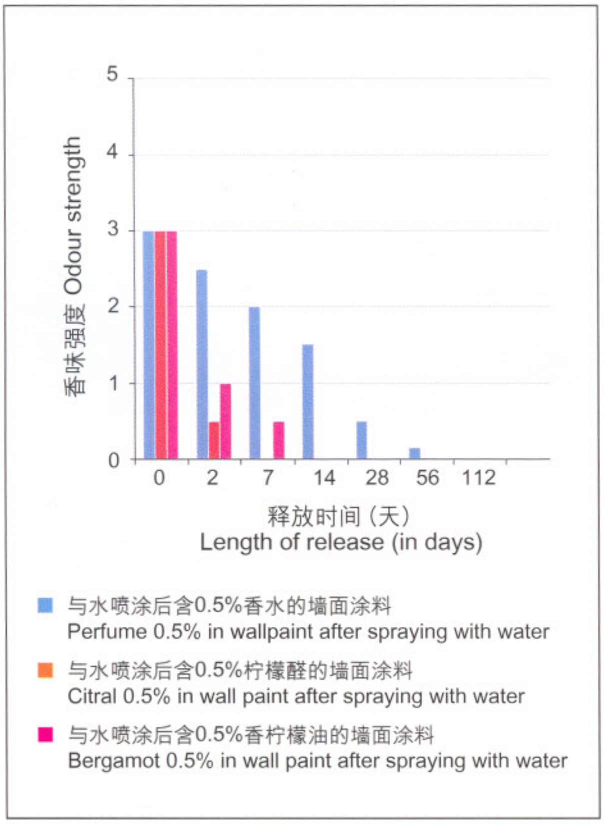

图1：聚合物乳胶涂料中简单香料物质的释放—香味评估(香味强度：5=气味强烈，0=没有气味)

Figure 1: Release of uncomplexed fragrances from a set polymer emulsion paint – odour evaluation (smell strength: 5=strong smell, 0=no smell)

anthranilate found in orange blossom oil repels birds. Indoor coatings might be used to improve the olfactory quality of ambient air and to ward off harmful or annoying insects such as mosquitoes. Moths, for example, steer clear of lavender blossom, and mosquitoes and horseflies avoid the smell of eugenol and geraniol. For several years, research institutes, particularly in tropical regions, have been looking for ways of using ethereal oils to protect against insects such as mosquitoes or termites – not least as a way of alternatively controlling or embanking malaria and yellow fever.

All applications could further benefit from antimicrobial characteristics, whether additionally or alternatively. Many ancient household remedies and increasing numbers of pharmaceutical preparations already make use of the antimicrobial effect of ethereal oils. For instance, several scientific studies have shown that the oil derived from red thyme is highly effective against both bacteria and molds. Therefore, a suitable fragrance could also be added to prevent fungal attack of the set material (lining, paint, coating, filler, sealant).

Until now, these types of application simply were not possible because the fragrances are highly volatile and chemically sensitive. Thus, many fragrances in coatings lose their odour after just a few days (**Figure 1**). For instance, several of their ingredients are oxidised by exposure to air and light; others are chemically changed by heat or the effects of acids or alkalis. This renders oils ineffective; in extreme cases, they are even transformed into harmful substances. Some components would not even withstand the shearing action of mixing them into the plaster-mortar paste or liquid wall paint. Though, as compensation, the oils and their components have another advantage: so far as is known, microorganisms do not develop resistance to essential oils.

For these reasons, a system is needed that protects the sensitive substances and releases them in a controlled manner over a long period of time only after the coating has dried and set. The German-based chemical company Wacker Chemie AG now has developed such a release system: it utilises the principle of molecular inclusion to enclose fragrances in cyclodextrin.

Essential oils & their constituents

A rich source of biologically effective fragrances are the volatile (ethereal or essential) oils obtained from plants or plant parts by steam distillation. Industry shows rising interest in these oils because they are made from renewable raw materials and at the same time have, as explained above, interesting biological effects.

Essential oils are blends of lipophilic materials. They contain predominantly terpenes, which are present in the form of alcohols, aldehydes, ketones, esters, lactones and hydrocarbons. To an extent depending on

香精油及其组成要素

通过蒸馏方法从植物或植物某些部分提取的挥发性香精油是获得生物效应香料的丰富来源。由于这些香精油是由可再生原材料获得并且同时也如前所述具有以上的生物效应，所以工业界对这些物质表现出日益高涨的兴趣。

香精油是亲脂性物质的混合物。它们主要的成分是萜烯，存在的形式包括醇类、醛类、酮类、酯类、内酯和碳氢化合物等。根据其组成成分，香精油很大程度上能够起到真菌杀灭剂、杀菌剂、杀虫剂和抗虫剂等作用。近年来，这些效应已经得到了充分的研究[1~4]。

尤其有效的抗菌物质包括肉桂皮油和柠檬草油以及从普通百里香(干百里香)中提取的百里香油。此外，还有效果稍弱的茶树油。百里香油(普通百里香)、丁香叶油和肉桂叶油具有非常显著的杀灭真菌的作用，茶树油和柠檬草油能够阻止真菌的生长。麝香草酚、丁香酚和柠檬醛也具有强烈的抗真菌作用。

萜烯的化学敏感性来自分子中的功能性基团：醛类容易被氧化；烯烃双键容易受到亲电进攻；碳链主键的支链可能会发生分子断链。

针对从澳大利亚茶树(Melaleuca alternifolia)中提取的茶树油，已经对保护其活性物质的措施的重要性进行了阐述[5]。这种无色至黄绿色的香精油是不同的单-和倍半萜(最重要的是萜烯-4-醇、α-萜烯、γ-萜烯和1,8-桉油素)的混合物。当与空气中的氧气和光线接触并且升高温度时，会导致活性物质萜烯-4-醇含量的显著减少但同时会增加过敏源(对伞花烃、含醇倍半萜 烯、过氧化物)的浓度[6]。活性物质的降解和一些非期望产品的形成可以通过适当的稳定性方法得以避免。

分子包合保护香料

环糊精内部的分子包合是一种稳定香料物质的新方法。环糊精是非还原的手性环状低聚寡糖物质。其分子中包含了一定数量α-(1,4)-糖苷连接至环上的α-D-葡萄糖单元。葡萄糖单元成为一个锥形(耦合)腔的环。腔体的内部是憎水性，而环糊精分子的外部则为亲水性(**图2**)。

一个由七个葡萄糖单元组成的β-环糊精分子在其内腔中可以容纳一个具有适当尺寸和外形的亲脂性香料分子，如一个单萜烯分子。这种包合化合物就称为主—从化合物并且是通过范德华力结合在一起。包合化合物的形成和分裂要求有水的存在。一个从属分子只要包合在内腔中，那么就不会再进入气相中也不会发生化学变化，同时也可以抵抗光和热的作用[7~9]。

their constituents, essential oils can act as fungicides, bactericides, insecticides and insect repellents. These effects have been studied thoroughly in recent years[1~4].

Particularly effective against bacteria are cinnamon bark oil and lemon grass oil, thyme oil obtained from common thyme (Thymus vulgaris) and – somewhat less effective – tea tree oil. A pronounced fungicidal effect is exerted in particular by thyme oil (common thyme), clove leaf oil and cinnamon leaf oil; in addition, tea tree and lemon grass oil can retard fungal growth. Thymol, eugenol and citral are strongly antifungal.

The chemical sensitivity of the terpenes stems from the functional groups in the molecule: aldehydes are susceptible to oxidation, olefinic double bonds are susceptible to electrophilic attack, and branches of the carbon backbone constitute possible sites for molecular scission.

The importance of measures to protect the active substances is illustrated by the case of tea tree oil[5], which is obtained from leaves of the Australian tea tree (Melaleuca alternifolia). This colourless to yellowish-green essential oil is a mixture of different mono- and sesquiterpenes (above all terpinen-4-ol, α-terpinene, γ-terpinene and 1,8-cineol). Exposure to atmospheric oxygen, light and elevated temperatures leads to a marked reduction in content of the active substance terpinen-4-ol but simultaneously increases the concentration of allergens (ρ-cymene, alcoholic sesquiterpenes, peroxide products)[6]. Degradation of the active substance and the formation of such unwanted products can be avoided by suitable stabilisation methods.

Molecular inclusion protects fragrances

Molecular inclusion inside a cyclodextrin is a new way to stabilise fragrances. Cyclodextrins are non-reducing, chiral, cyclic oligosaccharides. Their molecules consist of a certain number of α-D-glucose units linked α-(1,4)-glycosidically to a ring. The glucose units are arranged in such a way that the ring is a conical cavity. The inside of this cavity is hydrophobic, while the exterior of the cyclodextrin molecule is hydrophilic (**Figure 2**).

A β-cyclodextrin molecule composed of seven glucose units can host a lipophilic fragrance molecule of the right size and shape, such as a monoterpene molecule, in its cavity. Such an inclusion compound is called a host-guest complex and is held together by Van der Waals forces. Formation and dissociation of the inclusion compound require the presence of water. For as long as a guest molecule remains enclosed in the cavity, it cannot enter either into the gaseous phase nor undergo chemical change; it is also protected against light and heat[7~9].

On exposure to water, the complex dissociates and the guest – the enclosed fragrance molecule in our example – is released in chemically unchanged form. The rate of release is controlled by the level of exposure to water. After

当处于水中时，组合物就会开始分离，我们所列举的从属被包合香料分子就会以化学稳定的形态释放出来。释放的速度由与水接触的程度控制。从属分子释放后，空出的腔体就可以吸收其它具有合适尺寸和外形的亲脂性分子，例如具有难闻味道的亲脂性物质。因此可以用于消除厨房里以及香烟、腐烂物质和尿液的难闻气味。目前，一些用于掩蔽及消除难闻气味的全球性家用护理产品已经在使用这项技术，其原理就是控制释放香料并且吸附难闻气味物质。

现在，这项技术也可以被应用于建筑领域中。香料包合化合物可以用在设计为非憎水且不具有非抗水表面的聚合物石灰浆、涂料、油漆、刮浆材料和密封胶中。

香料释放

采用各种天然及合成香料物质，针对组合物对香料物质的稳定性影响进行了实验研究。考察的因素包括环境温度和40°C时的贮存稳定性以及耐光线性能。在所有研究中，都对β-环糊精包合组合物与“游离”从属物和环糊精物理混合物的行为进行了比较。

图3和**图4**是样品测试的结果。包合的香料甚至在长期接触热量、空气和光线后都能保持非常的稳定。在准备使用的水性分散体和非憎水材料中也达到了非常有效的保护作用。

release of the guest, the now empty cavity could absorb another lipophilic molecule of the right size and shape, such as a molecule of a foul-smelling lipophilic material, and thus eliminate unpleasant odours, for instance those in the kitchen, cigarettes, rotting material and urine. Several globally available home care products for masking and eliminating unwanted smells are already using this technology for the controlled release of fragrances and the absorption of foul-smelling substances.

Now this technology can also be put to service in the construction sector. There, the fragrance inclusion compounds may be used in those polymer-bound plasters, coatings, paints, screeding compounds and sealants that set to yield a non-hydrophobic and hence non-water-repellent surface.

Fragrance release

The influence of complexation on the stability of fragrances was studied experimentally on various natural and synthetic fragrances. Factors examined included storage stability at ambient temperature and 40°C, and light resistance. In all studies, the behavior of the cyclodextrin inclusion compounds were compared with that of a physical mixture of "free" guest and cyclodextrin.

Sample results are shown in **Figures 3** and **4**. The complexed fragrances generally proved to be very stable even after protracted exposure to heat, air and light. Effective protection is also achieved in the ready-to-use aqueous dispersions and in the set non-hydrophobic materials.

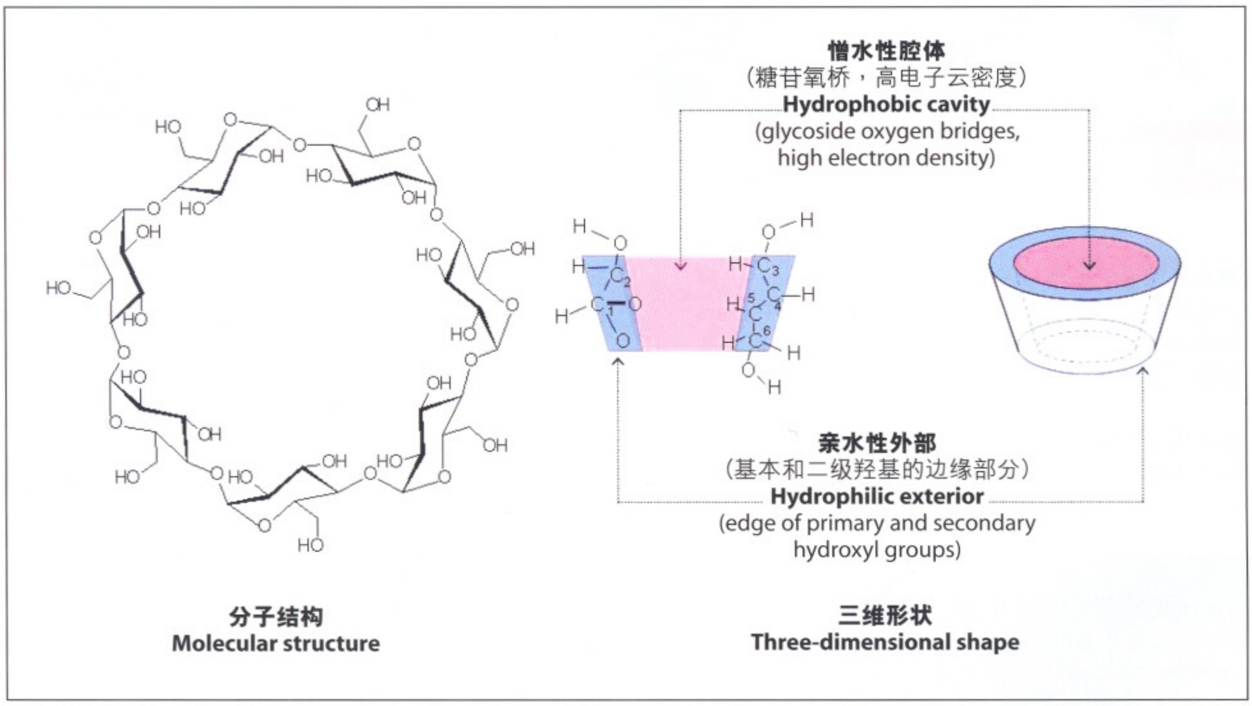

图2：β-环糊精的结构和分子形状
Figure 2: Structure and molecular shape of β-cyclodextrin

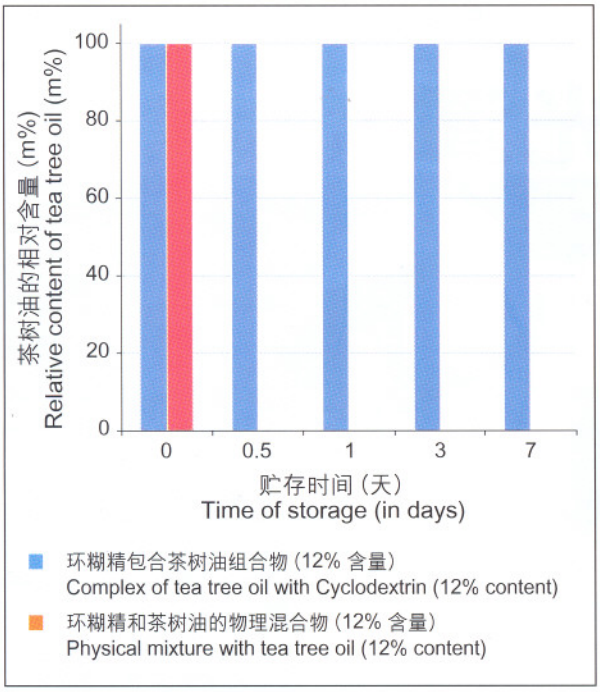

图3：黑暗空气中40°C条件下，包合组合物和游离茶树油(与环糊精物理混合)的稳定性

Figure 3: Stability of complexed and free tea tree oil (physical blend with cyclodextrin) with 40°C in the dark under air

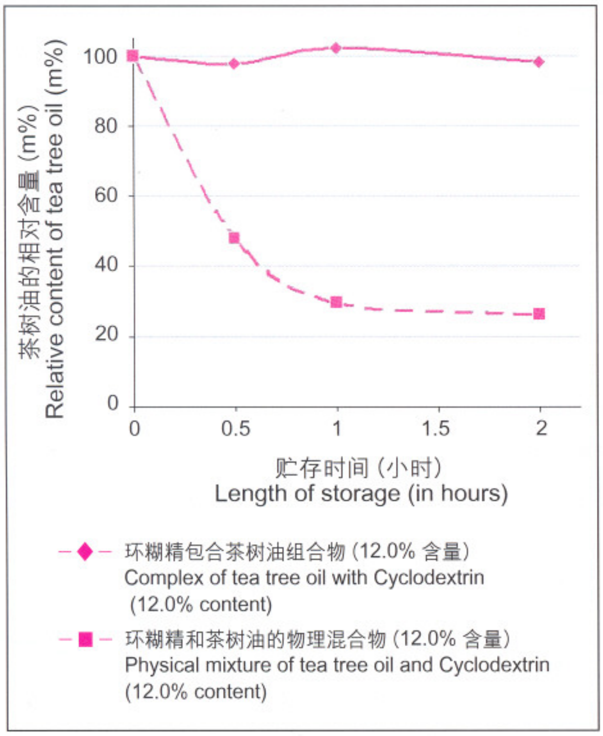

图4：在UV灯(阳光测试仪器，Atlas材料测试方法)的辐射2小时，物理混合的茶树油含量下降至26%而包合组合物中含量仍为100%

Figure 4: On irradiation with UV light (Suntest instrument, Atlas Material Testing Solutions), the tea tree oil content in the physical mixture drops to 26% within 2 hours while it is still 100% in the complex

Release of the fragrance – and thus of the biologically active ingredient – begins when water makes contact with the set, dried material containing the fragrance complex (the materials could be a lining, coating, paint or sealant). In order that release could be studied under practical conditions, a typical polymer emulsion paint was made that contained a cyclodextrin fragrance complex apart from the usual components (such as film-forming polymer dispersion, fillers, titanium dioxide as pigment, rheological additives, and dispersing and antifoam agents). The complex was added in quantities sufficient to produce an active ingredient content in the liquid formulation of 0.5% in each case.

The coating agents were applied evenly to a wall (rate: 150 g/m^2). They were allowed to dry and set before the fragrance release was measured analytically. Fragrance release was determined by means of gas chromatography. To this end, material was removed from the wall coating every 3 months. In each case, 500 mg of the material was examined by comparing the concentrations of the volatile materials in the headspace above the sample before and after addition of 100 mg water.

Sampling proceeded by means of SPME (solid phase microextraction)[10] in which the volatile constituents are collected from the headspace by adsorption on the surface of a silicone-coated plastic needle. The compounds are thermally desorbed from the needle in the injector of a gas chromatograph and separated chromatographically afterwards.

The area under the fragrance peak was selected as the measure of the quantity of fragrance released into the headspace; in the case of substance blends, the sum of the areas of all those peaks was determined which are assignable to the compounds contained in the blend originally used. These studies, too, confirmed that the release system works (**Figure 5**).

Subsequent Treatment & Areas of Application

The fragrance complexes of the natural β-cyclodextrin are available commercially. The inclusion compounds are in the form of white, free-flowing powders; methyl β-cyclodextrin complexes are also obtainable as aqueous dispersions or solutions. The natural cyclodextrins are produced exclusively from renewable raw materials. Furthermore, many fragrances, such as the essential oils, are obtained from plants.

All products can be incorporated readily into liquid and pasty aqueous dispersions. The result is a dispersion in which the fragrance complexes are homogeneously distributed (dispersions containing these cyclodextrin complexes for applications in the building sector have been patented). Neither high shear stress nor temperature rises cause premature release of the fragrance. Rather, the fragrance is released as a function of moisture content from the applied and set material.

当水与制备好的含有香料组合物的干燥材料(这种材料可以是饰面层、涂层或密封胶)接触时，能够产生生物效应的香料组分就开始释放。为了可以在实际条件下研究释放，制备了一个除了一些常用的涂料组分(如聚合物分散体作为成膜物资、填料和二氧化钛作为颜料体系、流变助剂以及分散助剂和消泡助剂)之外，还含有环糊精香料组合物的典型聚合物乳胶涂料。每个实验中，组合物的添加量为液态涂料配方的0.5%，足以产生活性作用。

涂层材料被均匀地施工在墙面上(150克/平方米)，在香料释放测试分析前被干燥和固定。香料的释放用气相色谱的方法进行测试。因此每三个月从涂层墙面上取出物质。在每次实验中，取出500微克物质进行测试，测试其加入100微克水之前和之后顶部空间挥发性物质的浓度。

用固相微萃取(SPME)[10]的方法处理样品，可以从顶部空间通过塑料覆硅探针表面上的吸附收集可挥发性组分。在气相色谱分析和后面的分离色析的注射器中，吸附物从探针中会受热释放。

香料最高峰的面积被选为测定释放进入顶部空间的香料的量。在混合物质中，测试所有峰的面积总和，这些峰分别归属于原先所使用的混合物包括的物质。这些研究也证实释放系统在发挥作用(**图5**)。

后续处理及应用领域

天然β-环糊精的香料组合物已经可以商业应用。这种包合组合物是白色自由流动的粉末。甲基β-环糊精组合物也可以制备为水性分散体或溶液的形态。天然环糊精香料组合物由可再生的原材料制备。此外，许多香料(如香精油)都是从植物中提取得到。

所有产品都可以稳定地应用到液态或浆状水性分散体中。其结果是能形成一个分散体，其中香料组合物被均匀稳定分散(应用于建筑领域的环糊精组合物分散体已经申请了专利保护)。高剪切应力和温度升高均不会导致香料的过早释放。此外，香料释放也与所应用材料中水分含量相关。

采用这种方法，石灰膏、油漆和其它涂料以及密封胶都可以为客户提供额外的功能性。目前，一些建筑材料的制造商正在对不同气候条件下使用香料环糊精组合物的实际性能进行监测。在亚热带地区，正在对散发出驱赶蚊子气味的涂料进行测试，早期的结果显示非常理想。这也是首次，建筑领域可以应用香料的嗅觉和生物潜能，应用自然产生的产品。

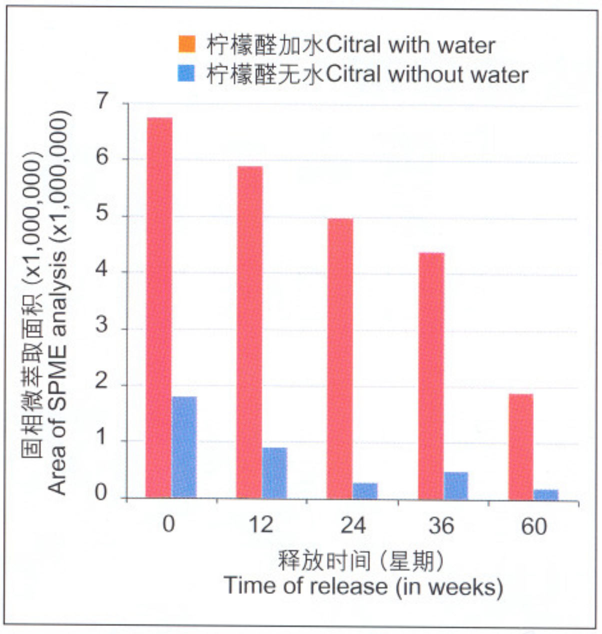

图5：柠檬醛从乳胶涂料中的β-环糊精柠檬醛组合物中受控释放-固相微萃取/气相色谱分析

Figure 5: Controlled citral release from a set emulsion paint via β-cyclodextrin citral complex – SPME/GC analysis

In this way, plasters, paints and other coatings as well as sealants can be given an additional custom-made functionality. At present, several manufacturers of building materials are for example examining the practicability of using the fragrance cyclodextrin complexes under different climatic conditions. In tropical Asia, for example, tests are being carried out on paints that emit a mosquito-repellent odour – early results are highly promising. For the first time, the construction sector can take advantage of the olfactory and biological potential of fragrances and avail itself of naturally occurring products.

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[10] A brief description may be found at www.evolution.uni-bonn/Chemie SPME.htm.