生物硅基功能性涂料光触媒对室内空气品质的改善（下）

Improving Indoor Air Quality Using a Biosilica-based Functional Paint & Coatings Photocatalyst (Part 2)

上期提到，Diatomix 公司开发了一种用于生物硅基光催化剂（已申请专利保护），该产品在添加到墙面涂料和地坪涂层中时可强力并持续地改善室内空气质量。通过去除挥发性有机污染物，该技术可以帮助抑过敏和疾病造成的不适。

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实验方法

合成技术

Diatomix 的合成工艺（正在申请专利）是强大且商业上可行的。我们已经开发能够使用多种金属有机钛前驱体的工艺。我们合成技术的关键是升温速率和温度控制。如**图 2** 所示，优化这些条件可以使离散的纳米颗粒优先沉积在硅藻壳的孔隙和内部。

VOC 的去除和降解测试

我们在美国三角研究园（RTP）实验室（美国北卡罗来纳州 Raleigh）进行了 VOC 去除测试。RTP 是与 Diatomix 签约的独立测试机构。方法如下：按照 ASTM 标准 D6670「室内材料 / 产品排放的挥发性有机物质的全室测定的标准实施规程」，通过将已知浓度的 VOC 引入到 LED 灯下的密封室中来测试样板对 VOC 的去除。第一个样品是用 Diatomix 的 Paint 08 和 Paint 011 两种乳胶涂料制备的，所述涂料在涂料研究集团公司（Coatings Research Group Inc., CRGI）（美国俄亥俄州克利夫兰）配制的，包含 10% 重量的 Diatomix 添加剂。每个样品各两磅直接从 CRGI 发送到 RTP。每个样品用两磅辊涂在两块石膏板上（尺寸为 1.2×2.4 米），石膏的背面和边缘用不会散发 VOC 的铝箔和 3M 箔带密封。都是根据 Diatomix 提供的样品制备说明进行的样品涂装（一道涂层两个小时后进行第二道涂层）。在第二次涂装 24 小时后，这些样板用于 VOC 降解测试。测试室耐化学腐蚀（体

As mentioned in the last issue, Diatomix Inc. has developed a patent pending, biosilica-based photocatalyst that actively and continuously improves indoor air quality when added to wall paint and floor coatings. By removing VOCs, the technology can help curb the discomfort associated with allergic symptoms and diseases.

Experimental methods

Technology synthesis

Diatomix's patent pending synthesis process is a robust and commercially viable procedure. We have developed the procedure to be able to use multiple metal organic titanium precursors. The key to our synthesis is the ramp rate and temperature holding points. Optimising these conditions allows the preferential deposition of discrete nano-particles in the frustule pores and interior as seen in **Figure 2**.

VOC removal & degradation testing

VOC removal testing was performed by Research Triangle Park (RTP) Laboratories (Raleigh, NC, USA). RTP is an independent testing facility contracted by Diatomix. Methods were as follows: Following ASTM standard D6670 "Standard Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials/Products", test panels were examined for removal of VOCs by introducing known concentrations of VOCs into the sealed chamber under LED light. First samples were prepared with two latex paints provided by Diatomix labeled Paint 08 and Paint 011, which were formulated at Coatings Research Group Inc. (CRGI, Cleveland OH) based on Diatomix additive at 10% by weight. Two quarts of each sample were sent directly from CRGI

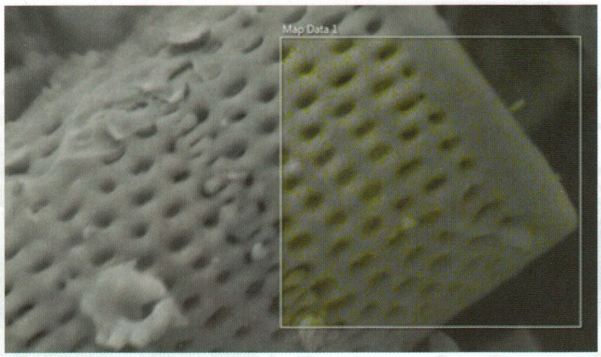


图 2：光催化颗粒修饰的硅藻扫描电子显微镜（SEM）图像和能量色散 X 射线光谱。
Figure 2: Scanning electron microscopy (SEM) of diatoms with energy dispersive X-ray spectroscopy of photocatalyst particles decorating the biosilica diatom.

积，1.2×1.2×2.4 米），由经过特殊处理的静电消散性透明丙烯酸表面制成。光源为 6T8 LED 灯（1.2 米长）固定装置组成，这些固定装置连接在朝向涂层测试面板的腔室外部。灯彼此间隔 40 厘米，最外面的灯距离测试室边缘 20 厘米。VOC 的去除测试是通过将涂装后的石膏板放置在测试室的一侧进行，而且其背面倾斜约 15 度。在引入 VOC 之前密封该腔室并平衡大约 45 分钟。在整个测试过程中监测温度、相对湿度和二氧化碳。测试前，预先测试显示腔室内没有挥发性有机化合物。然后，把甲醛（20ppm）和丁醇（20ppm）引入室中，并打开混合风扇 10 分钟。在 1、2、4、6 及 24 小时的时间点，通过 GC / MS 和 HPLC 对室内空气进行测试以确定测试室中的 VOC 水平。

VOC 矿化测试是在涂有 Diatomix 添加剂薄层的玻璃板上进行的。将四块玻璃板切成 25×8 厘米，用肥皂和水彻底清洗，然后在蒸馏水中冲洗 2 分钟。将 Diatomix 添加剂悬浮在由柠檬酸和乙二醇制成的聚酯溶液中。然后使用玻璃棒将浆料沿着玻璃板向下拉制成 50μm 厚的一层。然后将该层物质在 500°C 焙烧 30 分钟以除去所有有机组分。测定涂层重量为 60mg。然后使板在本实验室的标准条件下平衡 24 小时。将 4 个样板放入一个 5L 的玻璃测试室中并密封。将挥发性有机化合物（VOC）注入到玻璃室中，并且使用甲烷化器和火焰离子化检测器改性的气相色谱仪监测 CO_2 和 VOC 水平。

涂料耐久性测试

采用在 VOC 降低测试中制备样板的方法，制备了两个更小（8×8 厘米）的带有 Diatomix 涂层和宣伟公司涂层的样板。将四个样板放在 UVC 灯下进行相同的老化测试。在指定的时间点取下样板，并进行如下粉化测试：将标准的 Scotch 300 胶带置于单一样板的未触碰角上，并将 2kg 橡胶软木底的重物放置在涂层的面层静置 30 秒，然后取下胶带并放在底面涂成黑色的载玻片上。将载玻片上的胶带样品的中心置于 USB 显微镜下并成像以获得标准的 6mm 直径图像。通过 ImageJ 软件 [36] 对图像进行分析，得出白色颗粒的百分比。

to RTP. Two pounds of each sample were used to coat two sheetrock panels (size, 1.2 × 2.4 meters) with paint rollers. The back and edges of the sheetrock were sealed with aluminum foil and 3M foil tape that does not emit VOCs. The paint samples were applied according to the sample preparation descriptions provided by Diatomix (one coat applied and a second coat two hours later). 24 hours later after the second coat of paint, the panels were used for VOC degradation test. The test chamber is a chemically resistant chamber (volume, 1.2 × 1.2 × 2.4 meters) made from specially treated static dissipative clear acrylic surface. The light source consisted of 6 T8 LED light (1.2-meters long) fixtures that were attached to the outside of the chamber facing inward towards the painted test panel. The lights were spaced 40 cm apart from each other and the outermost lights were 20 cm from the edge of the test chamber. VOC removal testing was performed by placing painted sheetrock panel in the test chamber on one side and leaned at approximately 15 degrees from the back surface. The chamber was sealed and allowed to equilibrate for approximately 45 minutes prior to introducing the VOCs. Temperature, relative humidity, and carbon dioxide was monitored throughout the tests. Pretests demonstrate no VOCs in the chamber prior to testing. Then, formaldehyde (20 ppm) and butanol (20 ppm) were introduced into the chamber and the mixing fan was turned on for 10 minutes. Chamber air were tested by GC/MS and HPLC at 1, 2, 4, 6, and 24-hour time points to determine VOC level in test chamber.

VOC mineralisation testing is performed by coating a glass panel with a thin layer of Diatomix additive as follows. Four glass panels were cut to 25 x 8 cm and thoroughly cleaned with soap and water followed by rinsing in a stream of distilled water for 2 minutes. A slurry of Diatomix additive was then suspended in a solution of polyester made from citric acid and ethylene glycol. The slurry was then drawn down the glass panel using a glass rod to make a 50 μm thick layer. This layer was then fired to 500 °C for 30 minutes to remove all organic components. The resulting layer was determined to be 60 mg gravimetrically. The panels were then allowed to equilibrate under standard conditions in our lab for 24 hours. The 4 panels were placed with a fan into a 5 L glass testing chamber and sealed shut. VOCs were injected into the glass chamber and both CO_2 and VOC levels were monitored using a gas chromatograph modified with a methanizer and flame ionisation detector.

Paint durablity testing

Two smaller panels (8 x 8 cm) of Diatomix and Sherwin-Williams paint were prepared identically to those prepared in VOC reduction testing. All four panels were placed under UVC lights and aged identically. Panels were removed at specified time points and tested for chalking as follows. A standard Scotch 300 piece of tape was placed on an untouched corner of a single panel and a 2-kg weight with a rubber cork bottom was placed on top of the paint and allowed to sit for 30 seconds. The tape was then removed and placed on a glass slide with the bottom side painted black. The center of the tape sample on the slide was placed under a USB microscope and imaged to obtain a standard 6 mm diameter image. The image was analysed via ImageJ software[36] for the percentage of white particulates seen.

Results

Research Triangle Park Laboratories (RTP) (Raleigh, NC, USA), tested two samples for Diatomix to determine the reduction

结果

三角研究园实验室 (RTP)（美国北卡罗来纳州罗利市）测试了两个降低 2-丁醇和甲醛的 Diatomix 样品。RTP 研究表明，用白色 LED 灯照射模拟环境测试室条件时，添加了 Diatomix 添加剂的平面涂料配方「Paint 08」（含有 Diatomix 添加剂的定制涂料配方）与 Paint 011（不含 Diatomix 添加剂的相同定制配方）相比，Paint 08 能够显著降低 2-丁醇和甲醛的浓度（**图 4**）。接触 3 小时后，Diatomix Paint 08 配方将 2-丁醇的浓度降低了 32%，甲醛降低了 56%。接触 24 小时后，Diatomix Paint 08 将 2-丁醇的浓度降低了 91%，甲醛降低了 92%。

使用光催化剂降解 VOC 可以使室内空气持续改善。通过降解副产物和形成二氧化碳来监测 VOC 的降解。已经测试了 Diatomix 添加剂对甲醇、二氯甲烷和异丙醇的降解和矿化。**图 5a** 显示甲醇降解成二氧化碳，**图 5b** 显示二氯甲烷降解成二氧化碳，**图 5c** 显示异丙醇降解成丙酮。丙酮是异丙醇氧化中的第一个副产物。从这些结果，我们看到非极性分子二氯甲烷比极性异丙醇或甲醇具有较慢的降解速率。这可能是由于非极性分子吸附过程较慢所致。考虑到非极性挥发性有机化合物的数量，我们正在继续寻找提高非极性分子矿化方法。

甲醇的完全矿化需要六次氧化。如果我们使用甲醇来确定添加剂在极性分子上进行单电子氧化的速度，我们就可以预测其它挥发性有机化合物的降解速度。预测结果如**图 5d** 所示。异丙醇氧化成丙酮是双电子氧化，通过甲醇的矿化预测 60ppm 的异丙醇完全氧化成丙酮需要 14 个小时。我们从测试中看到，16 小时后所有异丙醇都转化为丙酮，这支持了我们氧化速率的预测。另外，由于在我们的测试室中有大约 250 毫克的添加剂，我们可以测定每毫克我们的添加剂曝露在明亮照射的涂装墙壁上的甲醇去除率。我们看到，对于完全的甲醇矿化，1 毫克我们的技术产品可以每小时使

of 2-butanol and formaldehyde. The RTP study found that the Diatomix additive added into a flat paint formulation "Paint 08" (custom paint formulation containing the Diatomix additive) was able to considerably lower the concentration of 2-butanol and formaldehyde when illuminated with white LED lights in a controlled but simulated environmental test chamber and when compared with Paint 011 (same custom formulation without the Diatomix additive) (**Figure 4**). After 3 hours of exposure, Diatomix Paint 08 formulation reduced the concentration of 2-butanol by 32% and formaldehyde by 56%. After 24 hours of exposure Diatomix Paint 08 reduced the concentration of 2-butanol by 91% and formaldehyde by 92%.

The degradation of VOCs using photocatalysts allows for a continual improvement in indoor air. Degradation of VOCs is monitored via degradation byproducts and carbon dioxide production. Diatomix additive has been tested for the degradation and mineralisation of methanol, dichloromethane and isopropanol. **Figure 5a** shows the degradation of methanol to carbon dioxide, **Figure 5b** shows the degradation of dichloromethane to carbon dioxide and the **Figure 5c** shows the degradation of isopropanol to acetone. Acetone is the first by-product in the oxidation of isopropanol. From these results, we see that the nonpolar molecule dichloromethane has a slower degradation rate then polar isopropanol or methanol. This may be due to a slower adsorption process with non-polar molecules. Considering the number of non-polar VOCs we are continuing to look for ways to increase the rate of mineralisation on nonpolar molecules.

The complete mineralisation of methanol requires six oxidations. If we use methanol to determine the rate at which our additive can perform single electron oxidations on polar molecules we can then predict the rate at which other VOCs will be degraded. The predictions are shown in **Figure 5d**. Knowing the oxidation of isopropanol to acetone is a two-electron oxidation, the mineralisation of methanol predicts that the complete oxidation of 60 ppm of isopropanol to acetone should take 14 hours. We see from our testing that after 16 hours, all isopropanol has been converted to acetone, supporting our oxidation rate predictions. In addition, since

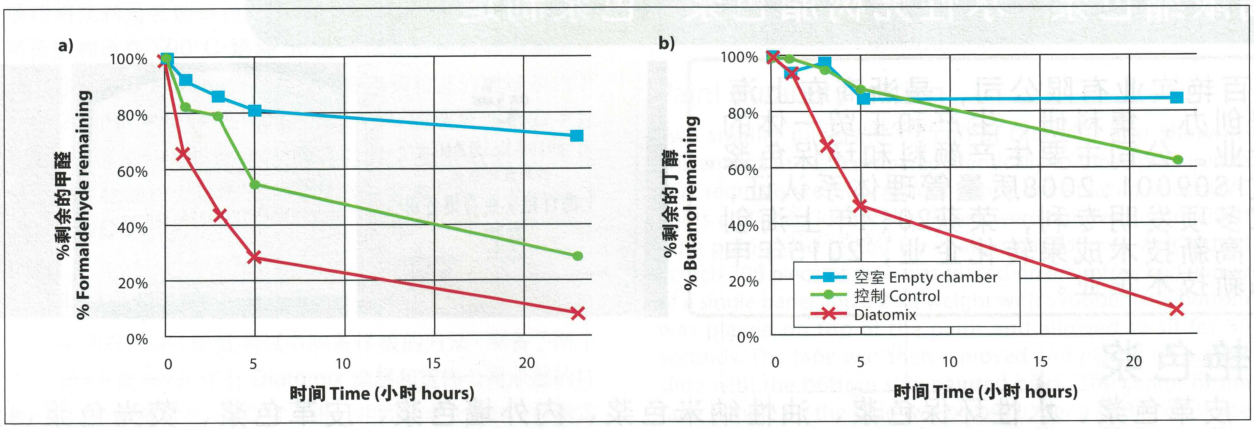


图 4：独立测试显示，在 3.62 立方米（132 立方英尺）的测试室内，一个侧面 1.2 x 2.4 米（4 x 8 英尺）涂装 Diatomix 涂料的干样板可以快速去除 VOC。在上述两图中，蓝色曲线数据（方块）= 对照数据（没有涂装涂料的测试室）；绿色曲线数据（圆圈）= 不含 Diatomix 添加剂的商用涂料涂装（Paint 011）；红色曲线数据（十字）= 含 Diatomix 添加剂的涂料涂装（Paint 08）。

Figure 4: Independent testing showing rapid removal of VOCs in a 3.62 m^3 (132 ft^3) testing chamber with one side of the chamber including a 1.2 x 2.4 m (4 x 8 ft) drywall panel painted with Diatomix Paint. In both figures above, blue line data (squares) = control data (chamber without a painted panel); green line data (circles) = contractor flat paint that does not contain Diatomix additive (Paint 011); red line data (crosses) = contractor flat paint containing Diatomix additive (Paint 08).

5ppb（十亿分之一）的甲醇完全矿化。使用**图 5d** 可以预测其它 VOC 初始去除率。

Diatomix 已经进行了挥发性有机化合物去除的重复性测试，以及我们涂料与竞争对手产品的耐久性测试。**图 6a-c** 显示了与含沸石添加剂的宣伟公司 Harmony 涂料和含专有的可见光催化剂的 Sto 公司 Climasan 产品相比，在五个周期内去除甲醇的重复性。如**图 6a** 所示，使用 Diatomix 添加剂的涂料与 Sto 的 Climasan 产品系列相似。相比之下，宣伟公司 Harmony 涂料随着循环的增加不能阻止甲醇的增加。

图 6d 显示了 Diatomix 公司 Paint 08 和宣伟公司 Harmony 涂料的长期 UVC 老化。我们可以看到，两种涂料都在紫外线照射的 86~170 小时之间开始出现粉化。这表明，Diatomix 技术的光催化行为不会降低涂料的使用寿命。Diatomix 添加剂在不降低涂料使用寿命和耐久性的情况下快速重复去除 VOC 的能力，使功能性涂料添加剂有望改善室内空气质量。

结论

用光催化剂如二氧化钛修饰硅藻可以提高光催化活性。硅藻充当光俘获结构并且可以聚集长波紫外线以及蓝色和红色的光波。使用这些波长光的催化剂，例如二氧化钛并将其可以固定在硅藻支撑结构上，由于入射光子的增加，可以表现出活性的增加。

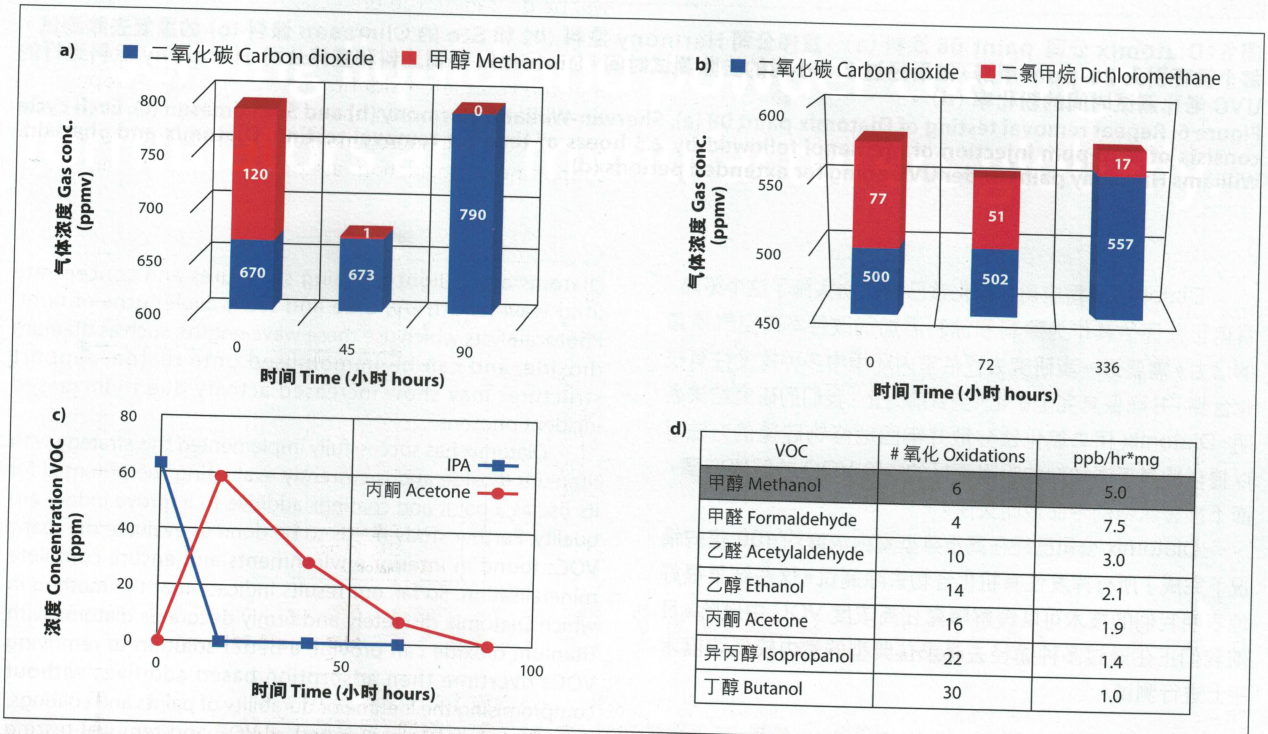
there was approximately 250 mg of additive in our test chamber we can determine the rate of methanol removal per mg of our additive exposed on the surface of a painted brightly illuminated wall. We see that for the complete mineralisation of methanol, 1 mg of our technology can completely mineralise 5 ppb of methanol per hour. Using **Figure 5d** other initial VOC removal rates can be predicted.

Diatomix has tested repetitive removal of VOCs and the durability of our paint vs. our competitors. **Figure 6a~c** shows the repetitive removal of methanol over five cycles vs. Sherwin-Williams Harmony paint, which contains zeolite additives and Sto's Climasan, which contains a proprietary visual light catalyst. As can be seen in **Figure 6a** paint with Diatomix additive performed similar to Sto's Climasan product line. In contrast, Sherwin-Williams Harmony was unable prevent the increase in methanol with increasing cycles.

Figure 6d shows long-term UVC aging of Diatomix Paint 08 and Sherwin-Williams Harmony. We can see that both paints begin to show increased chalking between 86 to 170 hours of UVC irradiation. This suggests that the photocatalytic behaviour of Diatomix technology is not degrading the paint binder and reducing lifetime. The ability of Diatomix additive to quickly and repetitively remove VOCs without reducing the paint lifetime and durability makes for a functional coating additive with promise to improve indoor air-quality.

Conclusion

The decoration of diatoms with a photocatalyst such as titanium dioxide can lead to increased photocatalytic activity.



VOC	# 氧化 Oxidations	ppb/hr*mg
甲醇 Methanol	6	5.0
甲醛 Formaldehyde	4	7.5
乙醛 Acetylaldehyde	10	3.0
乙醇 Ethanol	14	2.1
丙酮 Acetone	16	1.9
异丙醇 Isopropanol	22	1.4
丁醇 Butanol	30	1.0

图 5：甲醇（a）和二氯甲烷（b）完全矿化成二氧化碳需要明显不同的时间。异丙醇氧化成丙酮的时间少于 16 小时，但丙酮的完全氧化大约需要 90 小时（c）。甲醇的矿化速率被用来预测其它挥发性有机化合物的去除速率。

Figure 5: The complete mineralisation of methanol to carbon dioxide (a) and dichloromethane (b) requires considerably different timeframes. The oxidation of isopropanol to acetone takes less than 16 hours but the complete oxidation of acetone takes approximately 90 hours (c). The mineralisation rate of methanol is used to predict the removal rate of other VOCs.

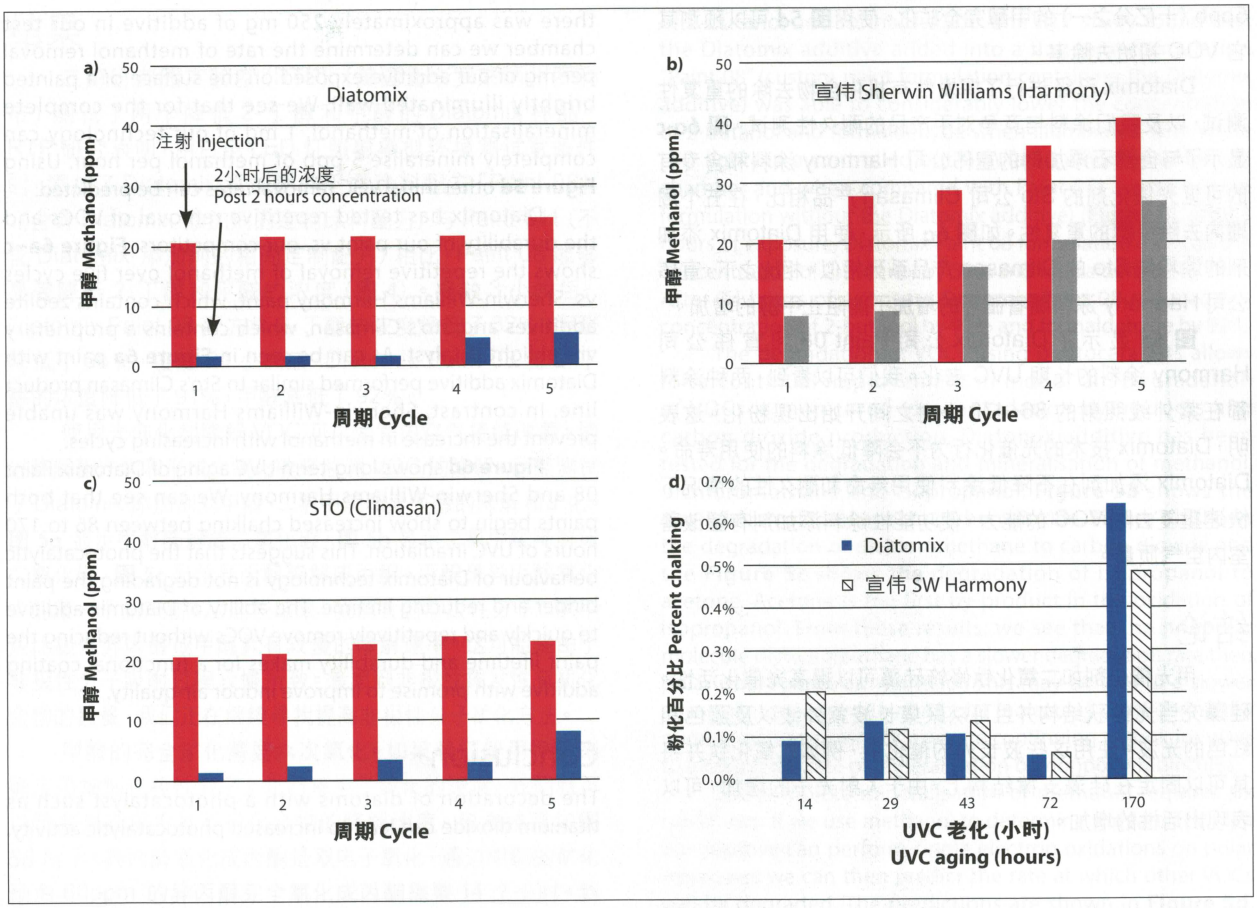


图 6：Diatomix 公司 paint 08 涂料 (a)、宣伟公司 Harmony 涂料 (b) 和 Sto 的 Climasan 涂料 (c) 的重复去除测试。每个循环引入 20-ppm 甲醇，然后经过 2.5 小时的去除测试时间。Diatomix 公司涂料和宣伟公司 Harmony 涂料进行的 UVC 老化测试时间的粉化率 (d)。

Figure 6: Repeat removal testing of Diatomix paint 08 (a), Sherwin-Williams Harmony (b) and Sto Climasan (c). Each cycle consists of a 20-ppm injection of methanol followed by 2.5 hours of time for removal testing. Diatomix and Sherwin-Williams Harmony paint under UVC aging for extended periods (d).

Diatomix公司应用二氧化钛已经成功实施了这个策略，目前正在评估其作为涂料和涂料添加剂改善室内空气质量的潜力。需要进一步研究去评估室内环境中多种挥发性有机化合物，并确保其完全矿化。到目前为止，我们的研究结果表明，Diatomix 用二氧化钛分散并牢固地修饰硅藻的方法可以提供比基于添加剂的吸附更好的去除 VOC 的解决方案，而不损害涂料的寿命或耐久性。

Diatomix 公司已经在高于典型室内浓度约 100 倍的情况下完成了所有挥发性有机化合物去除测试。这些结果很好地表明我们的技术可以缓解曝露在高浓度 VOC 中风险。目前我们正在通过多种途径去寻求在典型的室内较低浓度水平上进行测试。

参考文献 References

[36] Schneider, C. A.; Rasband, W. S. & Eliceiri, K. W. (2012), "NIH Image to ImageJ: 25 years of image analysis", Nature methods 9(7): 671-675, PMID 22930834 (on Google Scholar).

Diatoms act as light trapping structures and concentrate long wavelength UV, blue and red wavelengths of light. Photocatalysts which use these wavelengths, such as titanium dioxide, and can be immobilised onto diatom support structures may show increased activity due to increased incident photons.

Diatomix has successfully implemented this strategy with titanium dioxide and is currently evaluating the potential for its use as a paint and coatings additive to improve indoor air-quality. Further study needs to be done to evaluate the many VOCs found in interior environments and ensure complete mineralisation. So far, our results indicate that the method in which Diatomix discretely and firmly decorates diatoms with titanium dioxide can provide a better solution to removing VOCs overtime then adsorption based additives without compromising the lifetime or durability of paints and coatings.

Diatomix has performed all VOC and removal testing at concentrations approximately 100 times greater than typical indoor concentrations. These results are good for showing that our technology can mitigate high concentration exposures. We are currently pursuing lower concentration testing at typical indoor levels through multiple routes.