Laser imaging could offer early detection for at-risk artwork

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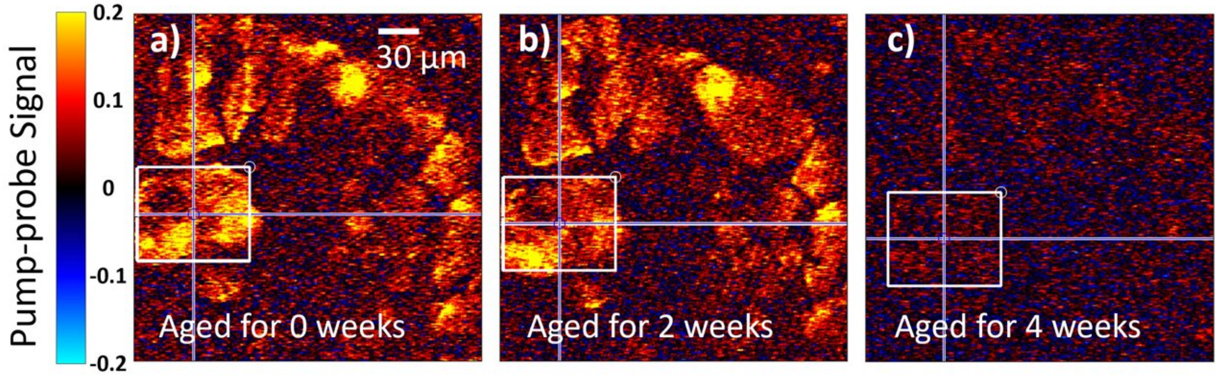

Images taken with a pump-probe microscope show how the paint samples fared over the course of the aging process. Areas that were unchanged are shown in blue, and areas where the cadmium sulfide has broken down are shown in red. Changes that were imperceptible to the eye were undeniable in the laser signal by as early as week one. Credit: Yue Zhou, Warren lab, Duke University.

Look closely at Impressionist paintings in museums compared with photos of them taken 50 years ago, and you might notice something odd: Some are losing their bright yellow hues.

Take the dramatic sunset in Edward Munch's famous painting "The Scream." Portions of the sky that were once a vivid orangish yellow have faded to off-white.

Likewise, some of the sunny yellow that Henri Matisse brushed between the reclining nudes in his painting "The Joy of Life" is now more of a drab beige.

Several other paintings from this period are facing similar issues. The bright yellow paint these artists used was made from the chemical compound cadmium sulfide. The pigment was beloved by many European artists of the late 19th and early 20th centuries. Claude Monet, Vincent van Gogh, and Pablo Picasso all brushed their canvasses with it.

"So many painters really loved this pigment," said Yue Zhou, who earned her Ph.D. in the lab of Duke chemistry professor Warren Warren.

But as the decades passed, many artists and art conservators realized they had a problem: Their cadmium yellow brushstrokes didn't look as vibrant as they once did.

The passage of time exposes artwork to light, moisture, dust and other elements of nature that can make pigments vulnerable to fading and discoloration.

In a new study, Duke University researchers show that a laser microscopy technique they developed could offer a means of early detection, making it possible to identify the first tiny signs of color change even before they're visible to the eye. The work is published in the *Journal of Physics: Photonics*.

Several techniques exist to study what pigments were used in a painting and how much they've broken down. But they typically involve scraping off a tiny chip of paint with a scalpel to analyze its composition. That method can damage the piece and limits the area to be studied, Zhou said.

"It's a little like surgery," she added.

Enter pump-probe microscopy. It can peer into layers of paint and detect chemical changes that mark the onset of a pigment's decay, without taking cross-sections of the original artwork.

The technique uses ultra-fast pulses of harmless visible or near-infrared light, lasting less than a trillionth of a second, and measures how they interact with pigments in the paint. The resulting signals can be used as chemical fingerprints to identify which compounds are present.

By focusing the laser beam at different locations and depths within the sample, the researchers are able to create 3D maps of certain pigments and monitor what's happening at scales as small as a hundredth of a millimeter.

For the new study, the researchers used pump-probe microscopy to analyze samples of cadmium yellow paint subjected to an artificial aging process.

In a lab on Duke's west campus, Zhou stirred up samples of the famous color. Taking a bottle of powdered cadmium sulfide pigment off a shelf, she mixed it with linseed oil and then brushed it on microscope slides to dry.

Some samples were left in a dark and dry environment, protected from moisture and light damage. But the rest were placed in a special chamber and exposed to light and high humidity—factors known to wreak havoc on unstable colors.

The researchers then imaged the paint samples using pump-probe microscopy to track the degradation progress on a microscopic scale.

Compared with control samples, the samples that got the aging treatment emerged looking the worse for wear. After four weeks in the aging chamber, they had faded to lighter shades of yellow.

But even before these changes became noticeable, clear signs of decay were already apparent in the pump-probe data, Zhou said. The cadmium sulfide signal started to wane as early as week one, eventually decreasing by more than 80% by week four.

The signal loss is a result of chemical changes in the pigments, Zhou said. Moisture triggers the transformation of cadmium sulfide, which is yellow, into cadmium sulfate, which is white—resulting in a whitish or dull cast.

Senior co-authors Warren and Martin Fischer had originally developed the technique to analyze pigments in human tissue, not works of art—to inspect skin moles for signs of cancer. But then they realized the same approach could be used for art conservation.

There is a caveat: While the technique spots early changes in a nondestructive way, conservators can't easily recreate the bulky laser setup in their own museums. In the future, the team says it might be possible to develop a cheaper, more portable version that can be used to study paintings that are too vulnerable or large to transport and analyze off site.

Of course, any color loss that has already happened can't be reversed. But one day, art conservators might have a new tool to spot these changes earlier and take steps to slow or stop the process in its beginning stages.

The research has potential applications beyond artists' pigments. Looking at cadmium yellow degradation in century-old paintings could help researchers better understand modern materials that are vulnerable to the elements too, such as the cadmium sulfide used in solar cells, Warren said.

More information: Yue Zhou et al, Non-destructive three-dimensional imaging of artificially degraded CdS paints by pump-probe microscopy, *Journal of Physics: Photonics* (2024). DOI: 10.1088/2515-7647/ad3e65

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