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X-ray allows a new step in the understanding of why several paintings by well-known late 19th century and early 20th C. artists such as Henri Matisse lose their yellow shine

With support, in part, from the Mellon Foundation and the Lenfest Foundation, the Barnes Foundation worked with other major art museums and an international and multidisciplinary team of American and European scientists, involving the ESRF, to study several paintings of Henri Matisse, James Ensor and Vincent Van Gogh, among others, in order to understand the discolouration and physical deterioration of a bright yellow pigment called cadmium yellow. Commonly used by the Impressionist, post-Impressionist, and early modernist painters, over time cadmium yellow pigment loses its vibrancy, turns into a beige or grey substance, and in the worst cases starts to fall away from the canvas. The research results reveal not only the chemistry of the discolored paint, but also the chemistry used to prepare the paints that were available to the turn of the 20th century's most treasured artists. This information is vital for the preservation of the masterpiece of our cultural heritage and also helps to identify degradation at an earlier stage. Indeed, over the past decade there has been a growing realisation among museum scientists that this disfiguring phenomenon is affecting billions of dollars of our global cultural heritage. This study has been published in Applied Physics A.

In paintings such as 'The Joy of Life' by Matisse and 'Flowers in Blue Vase' by Van Gogh, discoloration of the cadmium yellow pigment has caused the general appearance and color balance of the painting to be significantly altered. This is especially the case in 'The Joy of Life', in the collection of the Barnes Foundation, a fine arts museum in Philadelphia, PA, USA where large, originally bright yellow areas have now acquired an ochre-beige tint.

The team employed a combination of methods such as X-ray diffraction, X-ray absorption spectroscopy, X-ray fluorescence analysis and infrared microscopy on tiny samples of damaged paint removed from the works. These very sensitive methods of investigation based on synchrotron radiation were used to examine minute paint fragments obtained from several paintings by well-known late 19th Century artists such as Henri Matisse, Vincent Van Gogh and James Ensor. These layers can be as small as 1/100th of the thickness of a human hair but their presence can dominate the visual appearance of a painting, severely distorting the artist's original intent.

"*The main challenges associated with the analysis of such materials are the very limited amount of materials (far less than 1mm³) and their extreme complexity. This makes the use of synchrotron sub-micrometric probes essential*", **says Marine Cotte, responsible for the ID21 beamline at the ESRF, where most of the experiments were carried out**. *Such micro-fragments,* adds Marine Cotte*, are usually made of various ingredients (the ones introduced by the painter, on purpose or unknowingly, and those related to degradation or to later conservation) and of various natures (from very well crystallised to amorphous compounds, from inorganic pigments to organic binders…) all associated in a complex micro-stratigraphy. The ID21 beamline provides many analytical techniques (based on X-ray and infrared light) but the application of such beams to such samples is not straightforward.*

ESRF - Contact presse : press@esrf.fr - +33 4 76 88 26 04
Delphine Chenevier, Head of communication, delphine.chenevier@esrf.fr - +33 4 76 88 26 04

A PhD thesis, led by Emeline Pouyet, first author of the work, was dedicated to optimise all steps of the experiments, from the implementation of strategies for sample preparation, to the full data analysis, integrating results from all experiments (elemental, molecular and structural composition). Most of the techniques were used in micro-mapping mode, meaning that the compounds can be not only identified but also localised. This is particularly important to determine if they come from the pigment primarily used by the painter, or if they are related to further degradation."

Fig. 1 **a** Henri Matisse, French, 1869–1954 *The Joy of Life*, between October 1905 and March 1906, oil on canvas, 69½ × 94¼ in. (176.5 × 240.7 cm), oil on canvas, The Barnes Foundation, BF719; **c** *upper left* zoom showing tan-brown alteration crusts on the yellow foliage and on the yellow fruit in the tree at the *upper right*, and zoom on the *faded* region below the central reclining figures, sampling locations for this study are represented by *black cross*; **b** Henri Matisse, French, 1869–1954 *Flower Piece*, 1906, 21 7/8 × 18¼ in. (55.6 × 46.4 cm), oil on canvas, The Barnes Foundation, BF205; **d** altered (*brown*) and non-altered (*yellow*) regions of yellow paint to the right of the pitcher, sampling locations are represented by *black cross*

The research team found out that the original chemical compound, cadmium sulphide, highly water-insoluble and bright yellow, is subject to a light-induced oxidation process. This transforms it into a very water soluble cadmium sulphate, which is colorless. This cadmium compound was previously encountered on the surface of an Ensor painting called "Still Life with Red Cabbage".

However, the cadmium in this soluble salt may react with other degradation products of the paint. For example the beige mineral otavite (cadmium carbonate) may be formed in this manner. The carbonate in this compound may result from the degradation of the oil that binds the paint. In some areas of 'The Joy of Life', a ivory coloured discoloration was observed that strongly resembles one encountered in the painting 'Flowers in a Blue Vase' by Vincent Van Gogh, where a combination of the transparent-grey mineral anglesite ($PbSO_4$) and the equally transparent cadmium oxalate was encountered. In addition, unmistakable evidence was found that Matisse sometimes and likely unknowingly used cadmium yellow paint that inevitably degraded over time. This paint contained substantial residues of the chemicals that were still used in the late 19th Century to create cadmium yellow. Upon degradation, causing the yellow cadmium sulphide to disintegrate, the more stable beige-coloured cadmium carbonate can be left behind.

« *As a chemist, I find it striking that in paintings of different artists and different geographical origins that (presumably) were conserved for ca 100 years in various museum conditions, very similar chemical transformations are taking place. This will allow us to predict with higher confidence what may be happening to these works of art in the coming decades.*" **says Koen Janssens, Professor from the DEpartment of Chemistry, University of Antwerp (Belgium)**.

"*The results of this study reveal how critical it is to understand not only the chemistry of the discolored paint, but also the chemistry used to prepare the paints that were available to the turn of the 20th century's most treasured artists*", **says Jennifer Mass, head of the research team, Senior Scientist at the Scientific Research and Analysis Laboratory of the Winterthur Museum (Delaware, USA) and associate professor at the Programme on Art Conservation of the University of Delaware,** "*When we combine our findings on the works of Henri Matisse with the studies carried out on works by Vincent Van Gogh and James Ensor our preservation priorities for these works becomes clear. Our understanding of their degradation has given us a 'road map' to guide us in the preservation of these works for the enjoyment and education of future generations. It also provides us with the information needed to digitally restore the damaged paintings, creating a computer-generated image that reveals the artists' original intent for the work. Such research preserves and protects not only the paintings themselves, but also the legacy of the artists who created them, allowing their original intentions to be understood and studied. While the damage that has occurred to the cadmium yellow paint cannot currently be reversed, the current study has pointed the way to several important areas that require further investigation. One of the most critical of these is developing a protocol for identifying the 'at risk' paintings that are in their earliest stages of degradation, even before it is visible to the naked eye, so that such works can be placed in the proper display and storage environments that will prevent the degradation from worsening*." The results permit preventive conservation measures such as closer management of in-museum light and relative humidity levels to be implemented, aimed at slowing down or even stopping the naturally occurring but undesired chemical transformations.

The research team was headed by Dr. Jennifer Mass, Senior Scientist at the Scientific Research and Analysis Laboratory of the Winterthur Museum (Delaware, USA) and associate professor at the Programme on Art Conservation of the University of Delaware. The team also comprised scientists from the Universities of Antwerp (Belgium), Utrecht (Netherlands), Washington and Lee University (USA) as well as from the 'Commissariat à l'énergie atomique et aux énergies alternatives' (CEA, France) and two synchrotron radiation facilities, the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and Stanford Synchrotron Laboratory (SSRL, CA, USA). Funding for the research was provided in part by the Mellon Foundation and the Lenfest Foundation through grants to the Barnes Foundation, Philadelphia, PA.

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About the ESRF:
The ESRF – the European Synchrotron – is a large scale international research instrument. It is the world's most intense source of X-rays. The extremely bright light that the ESRF provides to scientists from around the globe enables them to explore matter in many disciplines. Founded in 1988, the ESRF is a model of European and International cooperation with 21 partner countries, of which 13 are Members, and 8 are Scientific Associates. In 2009, the ESRF embarked upon an ambitious renovation programme worth 330 M€, the Upgrade Programme phases I and II. This programme has devised a new generation of synchrotrons and will enable its users to push the limits of scientific exploration of matter.

ESRF - Contact presse : press@esrf.fr - +33 4 76 88 26 04
Delphine Chenevier, Head of communication, delphine.chenevier@esrf.fr - +33 4 76 88 26 04