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Raman identification of yellow synthetic organic pigments in modern and contemporary paintings: Reference spectra and case studies

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Abstract

The characterization of the binding media and pigments in modern and contemporary paintings is important for designing safe conservation treatments, as well as for determining suitable environmental conditions for display, storage and transport. Raman spectroscopy is a suitable technique for the in situ non-destructive identification of synthetic organic pigments in the presence of the complex binding media characteristic of synthetic resin paints or colour lithographic inks. The precise identification of a pigment by comparing its spectrum to that of a reference is necessary when conservation treatments with aqueous solutions or organic solvents are being considered for a work of art, since solubility properties can sometimes vary within the same pigment group. The Raman spectra of 21 yellow synthetic organic pigments, belonging to the monoazo, monoazo lakes, diarylide, disazo condensation, benzimidazolone, bisacetoacetarylide, azo-methine metal complex, isoindolinone and isoindoline groups are presented. Since modern artists frequently mixed paint developed for other applications, in addition to colorants developed as artists' paints, other synthetic organic pigments were included in the spectral database. Two monoazo pigments, Pigment Yellow 1 and Pigment Yellow 3, a benzimidazolone, Pigment Yellow 154 and a phthalocynanine, Pigment Green 7, were identified in sample cross-sections from four modern and contemporary paintings in the collection of The Museum of Modern Art in Ljubljana, Slovenia.

Keywords: Raman database; Synthetic organic pigments; Modern art; Contemporary art

1. Introduction

After 1930, a variety of synthetic resins, such as acrylic, alkyd, polyvinyl acetate and nitrocellulose, were developed for different applications and later found their way into artists' paints. These resins, together with the variety of synthetic organic pigments developed after the second half of the 19th century, and numerous additives, such as surfactants, thickeners, defoamers, pH buffers, etc., resulted in complex paint formulations that require different approaches to their conservation from the ones developed for Old Master paintings. Widely used acrylic paint emulsions have good drying and mechanical properties, though they have a low glass transition temperature that makes them sticky and to have a tendency to accumulate air pollutants [1]. Water and many of the organic solvents commonly used to treat oil paintings can have drastic consequences in modern paint layers, such as swelling and dissolution of some of the paint components [1].

Pigments and surfactants in the paint formulations are considered to affect significantly the ageing behaviour and stability of modern paint layers to a wide variety of effects such as light, temperature and relative humidity [2–4]. In addition, modern artists mixed materials in their formulations that were not initially intended for artists' use, such as paint developed for other applications [2]. Because of this, conservators of modern paint are faced with complex systems in which all components have to be taken into account and, therefore, a detailed identification of the binding media and pigments needs to be carried out as a prerequisite for any conservation intervention as well as for determining suitable environmental conditions for display, storage and transport.

In addition to this, the identification of synthetic organic pigments can also help to determine whether a work of art has been

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re-worked at a later date and, in some cases, it can help the visual and stylistic examinations to detect forgeries.

Raman spectroscopy has proved to be suitable for the non-destructive identification of pigments in works of art and several databases had been compiled for the purpose [5–7], since the technique ultimately relies on a comparison of the spectrum of the unknown with that of a reference compound. In the case of the synthetic organic pigments in modern and contemporary works of art, a difficulty is often presented to conservation scientists due to the fact that some of these pigments, particularly the earlier ones, are no longer commercially available. A protocol to identify the sub-group an azo pigment belongs to has been proposed [7], though the precise identification of the colorant used is, in most cases, crucial to assure a proper conservation intervention since properties such as solvent-sensitivity can widely vary within the same pigment group.

The nature and position of the substituents in the aromatic rings influences the pigment solubility properties. Long-chain alkyl, alkoxy, alkylamino and sulfonic acid functions tend to increase the colorant solubility, while the presence of substituents like carbonamide groups, and possibly nitro groups or chlorine for azo pigments, hetero atoms, especially nitrogen, and to a lesser extent chlorine and bromine in polycyclic pigments, will decrease the solubility. The correlation between constitution and solubility has been studied, for example, for a selection of Naphthol AS pigments. It was found that the position of identical substituents in the aromatic ring of the diazo component controls the solubility. The larger the capacity of a pigment to form intermolecular hydrogen bonds the lower its solubility. The polar character of pigments precipitated as salts, such as monoazo pigment lakes, BONA, and β-naphthol pigment lakes, gives them good solvent fastness; an increasing number of sulfo and/or carboxy groups for salt formation, makes them more solvent resistant [8].

By the end of the 19th century, synthetic organic pigments were gradually introduced into the market and started to replace inorganic pigments in artists' media, such as lithographic inks [9], where their main advantage was that they would allow to achieve hues not accessible using inorganic pigments alone. To the present, about 160 pigments have been mentioned in artists' colour catalogues and archives such as those from The Royal Talens, Schmincke, Winsor & Newton, Lefranc & Bourgeois, Ferrario and Liquitex, but the number of pigments that can be found in modern and contemporary works of art exceeds this number, because of the application of paints that were never intended specifically for artists' use, such as house or industrial paints; today the total number of synthetic organic pigments listed for different applications in the Colour Index International exceeds 500; when also dyes are considered, the number of synthetic organic colorants listed is a few thousands [10]. In the present study, a reference spectral database of yellow synthetic organic pigments not previously published is presented, together with examples of synthetic organic pigments identified in paintings in the collection of The Museum of Modern Art in Ljubljana, Slovenia.

Members of the azo pigment group were among the first to enter the market at the end of the 19th century and, to this day, the group has remained as the largest commercially available [11]. The earlier azo pigments [8,10], that mostly came in red and orange shades, were prepared as insoluble salts of dyes, such as the β-naphthol pigment lakes, and BONA pigment lakes. Among them are: PY100, an aluminium salt of monoazopyrazolone, patented in 1884; the first monoazo yellow pigment, Hansa Yellow (PY1), introduced into the market in 1909; the diarylide yellow pigments, some of which have been patented as early as 1911 (e.g. PY12, PY13), and were first commercialized in 1935 and PY16, the first bisacetoacetarylide, discovered in 1921. The first disazo condensation pigments (e.g. PY95, PY128), that came into the market in 1954, were followed by the benzimidazolone series (e.g. PY151, PY154) in 1960 and, in the late 1960s, by the azo metal complexes (e.g. PY150) and the azomethine metal complexes (e.g. PY129, PY153); members of isoindolinone and isoindoline classes (e.g. PY109 and PY110) followed in 1964.

A few pigments belonging to groups other than the azo were commercially available at the end of the 19th and the beginning of the 20th centuries. PY115, a quinoline, was discovered in 1882; PY18, a thiazol, was discovered in 1888 and PY11, a nitro pigment, was discovered in 1909. The last two pigments are not commercially available today [10].

2. Experimental

2.1. Samples

Reference samples of yellow synthetic organic pigments were supplied by the following manufacturers: SunChemicals, Schminke, Kremer, Clariant, Ciba, EcPigments, Ferrario, Ostacolor and Hoechst. The pigments are represented by their Colour Index (C.I.) generic names (i.e. PY that stands for Pigment Yellow) and a number.

For the characterization of yellow pigments in modern and contemporary paintings, microsamples were removed from four paintings in the collection of the The Museum of Modern Art in Ljubljana, Slovenia. Two samples (FNK1 and FNK2) were removed from the acrylic painting on canvas "*Krtine*" ("*Molehills*"), by Franc Novinc; two samples (SPI1 and SPI2) were taken from the acrylic painting on canvas "*I like Madonna and she likes me*", by Silvester Plotajs Sicoe; one sample (TSU1) was removed from an acrylic painting on wood by Tugo Sušnik and another one (ZMA1) from the oil painting on paper and hardboard "*Uspavanka ali tri krave za štiri*" ("*A Lullaby or Three Cows for Four*") by Živko Marušič. These microsamples were embedded in a polyester casting resin as cross-sections, then grinded and polished.

2.2. Instrumentation

The paint layers in the polished cross-sections were examined by optical microscopy using an Olympus BX60 microscope, and the results were recorded using a JVC 3-CCD video camera and by scanning electron microscopy (SEM, JEOL 5500 LV, Japan), while elemental analyses of selected areas of the samples were performed by energy dispersive X-ray spectrometry (EDS,