Journal of Analytical and Applied Pyrolysis 115 (2015) 175–183

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Pyrolysis gas chromatography mass spectrometry of two green phthalocyanine pigments and their identification in paint systems

Giulia Germinario[a], Inez Dorothé van der Werf[a,*], Luigia Sabbatini[a,b]

[a] Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via Orabona, 4, 70125 Bari, Italy
[b] Centro Interdipartimentale, Laboratorio di ricerca per la diagnostica dei Beni Culturali, Università degli Studi di Bari Aldo Moro, Via Orabona, 4, 70125 Bari, Italy

ARTICLE INFO

Article history:
Received 20 February 2015
Received in revised form 1 July 2015
Accepted 20 July 2015
Available online 26 July 2015

Keywords:
Copper phthalocyanine
Pyrolysis
Gas chromatography mass spectrometry
Paint

ABSTRACT

Copper phthalocyanine pigments are commonly used in modern paints, printing inks, plastics, leather, and synthetic fibres. Here, a systematic pyrolysis/gas chromatography–mass spectrometry study of two commonly used green copper phthalocyanine pigments (PG7 and PG36) was carried out. Pyrolysis temperatures ranging from 300 °C up to 800 °C were applied in order to study the pyrolysis products generated at each temperature. At temperatures above 700 °C very volatile products such as ClCN—for PG7 – and HBr, CH_3Br and BrCN—for PG36 – were relatively abundant, whereas at higher retention times a series of halogenated aromatic compounds could be identified.

Py/GC–MS of green acrylic and oil paint systems containing PG7 and PG36 was also performed in order to verify the possibility to detect low amounts of copper phthalocyanine pigments in complex matrices. Although not all the pyrolysis products of the reference green copper phthalocyanine pigments could be detected, efficient identification of these pigments could be accomplished thanks to the presence of specific markers.

1. Introduction

Phthalocyanines are heterocyclic compounds with a central hole capable to bind hydrogen or metal ions (Al, Fe, Co, Zn, Cu, Ni). They are commonly used in modern paints, printing inks, plastics, leather, and synthetic fibres. Other usages concern CD-DVD revetments, flexible, cheap and versatile photovoltaic cells, pharmaceutical applications like contrast agents and anti-tumor drugs, combustion cells [1,2] and, recently, preparation of carbon nanotubes by pyrolysis of iron phthalocyanines has been proposed [3].

Phthalocyanines possess an extensively conjugated aromatic chromophore yielding a blue–green colour with a very high molar absorption coefficient. Phthalocyanine blue (C.I. Pigment Blue 15), a copper phthalocyanine complex (CuPc) was developed in the mid-1930s.

The pigments object of this study are two green copper phthalocyanines (CuPc), PG7 and PG36. PG7, which was first manufactured in 1938, is synthesized by replacing most of the hydrogen atoms of PB15 with chlorine atoms, which influence the electronic structure shifting its absorption spectrum. Pigment Green 36 is another variant, in which some of the chlorine atoms are replaced with bromine atoms; a wide tonal range of greens to green-yellows can be obtained. The production of the chlorine/bromine CuPc PG36 dates back to 1959 [4].

Micro-Raman spectroscopy is most frequently applied to the characterisation of phthalocyanine pigments [5–9], in particular in works of art [10–13]. Pyrolysis gas chromatography–mass spectrometry (Py/GC–MS) has been used as well for the analysis of various classes of synthetic pigments and has proven to be a fast method for the identification of organic pigments that yield sufficiently volatile pyrolysis products, showing a good sensitivity for azo pigments [14–17]. Indeed, this technique is often employed for the characterisation of modern paint materials since it can provide information on polymers, dyes, pigments and additives [18–23]. Concerning the phthalo blues (PB15 series), Py/GC–MS is not very informative, because only a few non-specific fragments are generated. Typically, 1,2-benzenedicarbonitrile is produced. Its occurrence simply points to the presence of a CuPc pigment, but it cannot be employed for discrimination purposes [17]. This marker compound has been efficiently used for the determination of PG7 and PB15:3 in layered paint samples as has been reported in an interesting study on the application of laser Py/GC–MS for the identification and localisation of varnishes, binders and colourants [24]. Recently, Ghelardi et al. have found that, in addition to the characteristic 1,2-benzenedicarbonitrile, the pyrograms of the PB15 series contain *o*-cyanobenzoic acid that might be considered

* Corresponding author. Tel.: +39 0805442115/+39 3490889934.
E-mail address: inezdorothe.vanderwerf@uniba.it (I.D.v.d. Werf).

http://dx.doi.org/10.1016/j.jaap.2015.07.016
0165-2370/

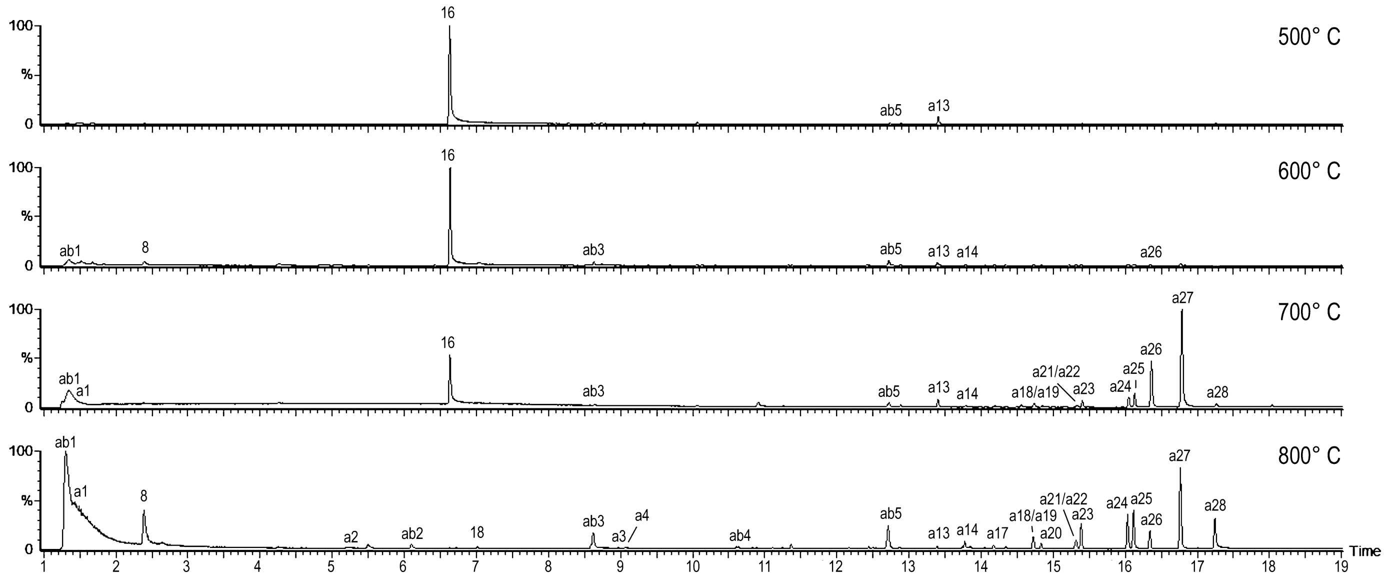

Fig. 1. Pyrograms of reference pigment PG7 (Kremer Pigmente) acquired at T_{py} = 500 °C, 600 °C, 700 °C and 800 °C.

as a marker and thus can aid in the identification of blue phthalos [16]. Green CuPc pigments, instead, may yield a higher number of specific pyrolysis products and a few of these have been recently reported [14].

In this paper we propose a systematic Py/GC–MS study of two commonly used green phthalocyanine pigments, PG7 and PG36. Pyrolysis temperatures ranging from 300 °C up to 800 °C were used in order to study the pyrolysis products generated at each temperature and to establish which of these temperatures provides the most informative pyrograms. Application to real ink and paint samples is also reported in order to demonstrate the potential of the proposed method to recognise phtalocyanine pigments in complex matrices.

2. Experimental

2.1. Materials

Two green phthalocyanine pigments, PG7 (C.I. 74260) and PG36 (C.I. 74265), were purchased from Kremer Pigmente GmbH & Co (Aichstetten, Germany) (Green Heliogen 23000 and Green Heliogen 23010) and from BASF (Ludwigshafen, Germany) (Heliogen Gruen L 8730 and Heliogen Gruen L 9361). A green pen marker, UNIPOSCA (tempera acrilica) (Osama S.p.a., Mombretto di Mediglia, Milan, Italy), two acrylic paints, *i.e.*, Brera Acrylic permanent green deep 340 (Industria Maimeri S.p.A., Mediglia, Milan, Italy) and Giotto Decor acrylic 531812 (F.I.L.A. Fabbrica Italiana Lapis ed Affini S.p.A, Pero, Italy), and two Rembrandt oil paints, phthalo green blue 680 and phthalo green yellow 681, from Talens (Apeldoorn, The Netherlands), were bought at a local retailer and applied on a glass slide, followed by solvent evaporation/drying for about two weeks.

Tetramethylammonium hydroxide (TMAH) (25% in H_2O) was purchased from Sigma Aldrich (Milan, Italy) and a 2.5% solution was prepared in methanol (Sigma Aldrich, Milan, Italy).

2.2. Py/GC–MS

The pyrolysis experiments were carried out with a microfurnace pyrolyser injection system Pyrojector II (SGE, USA). Small

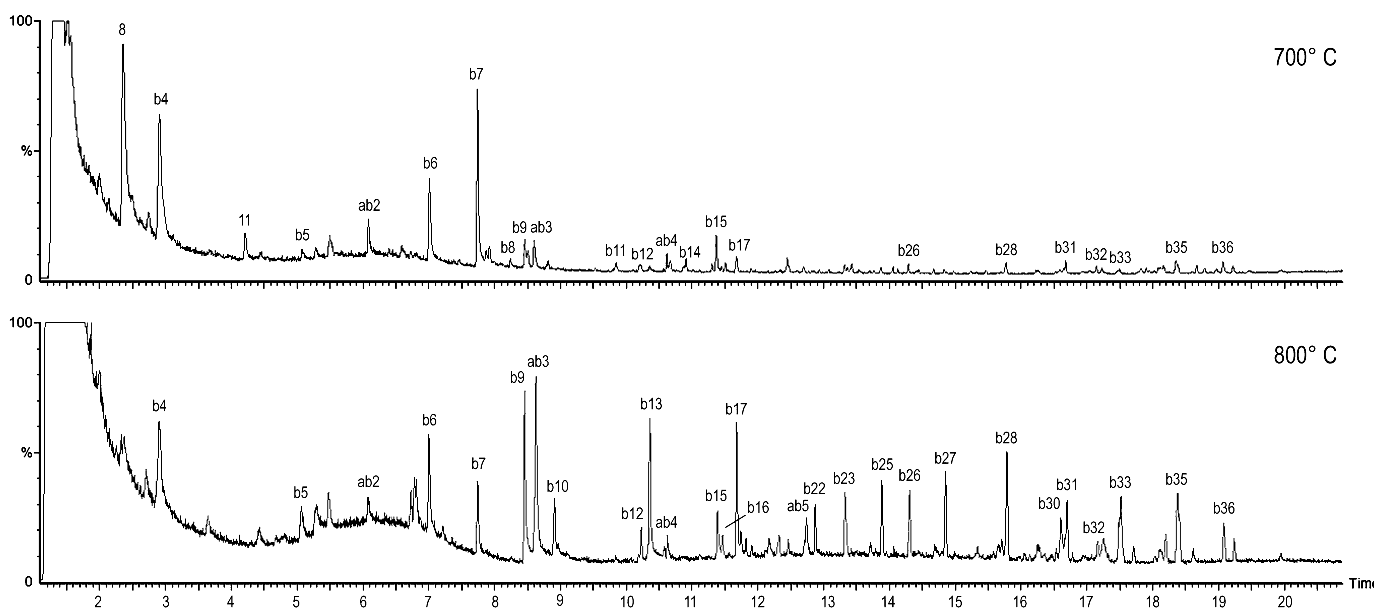

Fig. 2. Pyrograms of reference pigment PG36 (Kremer Pigmente) acquired at T_{py} = 700 °C and 800 °C.