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## **Chemical characterisation of spray paints by a multi-analytical (Py/GC-MS, FT-IR, $\mu$ -Raman) approach**

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### **Abstract**

This study outlines the chemical characterisation of ~~n. 45~~ a large number of commercial spray paints as used in street art, graffiti vandalism and for decoration purposes. The analyses were focused on the identification of the synthetic binding media, pigments and additives such as plasticisers and fillers, providing a data base as well as a methodological approach which could remarkably help investigations in a broad panorama of case studies, ranging from forensic science to cultural heritage. A protocol has been developed based on a multi-technique approach. In particular, Fourier Transform Infrared (FT-IR) spectroscopy, Pyrolysis/Gas Chromatography-Mass Spectrometry (Py/GC-MS) and  $\mu$ -Raman spectroscopy were applied and their strength and weakness points as to the identification ~~in~~ ~~order to identify~~ of all spray paints components are outlined. Each sample was first examined with FT-IR spectroscopy as a preliminary screening step to obtain indications on the main binder, which could then be confirmed and detailed using Py/GC-MS. Some pigments and extenders could be efficiently identified by examination of the FT-IR spectra and pyrolysis products. However, for most samples a  $\mu$ -Raman spectroscopy investigation was required in addition to the mentioned techniques in order to achieve the complete chemical characterisation of organic and inorganic pigments, extenders and fillers ~~was successfully accomplished with~~. Differences and common features among brands/colors are highlighted and discussed.

**Keywords:** spray paints, pyrolysis, GC-MS, FTIR,  $\mu$ -Raman

## 1. Introduction

Spray paints formulations are usually rather complex and can be associated to those of modern paints where, next to the binding medium and colouring matter, solvents, fillers, emulsifiers, antioxidants, plasticisers, light stabilisers, biocides and so on are commonly added (Pintus 2012, Learner 2004). Since these materials are prepared according to proprietary methods, the exact composition is often unknown, although this information may be very useful in the fields of forensic science and cultural heritage.

One case of forensic application is graffiti vandalism, where spray paints are used to blot or destroy various kinds of objects and buildings, sometimes of historic and artistic value. Spray paint analysis can lead, indeed, to identification of the brand name (or a list of brand names) and thus to a list of shops that distribute these spray cans (Govaert 2001, Burns 2000).

In the field of cultural heritage spray paints may be used for contemporary murals and paintings by famous artists such as Keith Haring and Banksy, or Richard Hamilton. Hamilton, for instance, has used automotive spray paints to depict an image of a car in a literal translation of the paint's intended use (Crook 2000). Identification of these materials may have a potential for dating and authenticity testing since the first synthesis of many pigments as well as their appearance on the market are well documented (Bouchard 2009, Brosseau 2009, Lutzenberger 2009). Moreover, determination of the chemical composition and study of the degradation mechanisms of modern (spray) paints may play an important role in the planning of conservation strategies and restoration treatments (Domenech-Carbò 1996, Ormsby 2013, Melchiorre Di Crescenzo 2014).

On the other hand, when spray paint graffiti are due to vandalism, the knowledge of their chemical composition may be essential for selecting the appropriate cleaning method in order to efficiently remove the materials without being harmful to the operators and to the substrate. Indeed, graffiti may be present on historical monuments and objects and in these cases preservation of the substrate materials and the use of compatible cleaning techniques is of extreme importance.

Nowadays, the procedures that are adopted to remove graffiti are mainly based on mechanical and/or chemical methods (Sanmartin 2014). Generally, mechanical cleaning makes use of air abrasion techniques which aim to remove the graffiti by abrading the surface with fine silica particles. Chemical methods usually include the use of organic solvents and alkali-based paint removers that can, however, be considered dangerous for the health and safety of the operator. At the same time solvent-based cleaning methods may be harmful for the treated objects, since they may cause a further penetration of the solubilised graffiti materials into the substrate. Recently, alternative methods for graffiti removal such as laser-based techniques (Van der Werf 2007, Gomez 2006, Chapman 2000, Rivas 2012) and biocleaning (Giacomucci 2012, Germinario 2014) have been proposed.

As to the chemical characterisation of spray paints, their complex composition requires a multi-technique approach in order to identify all components. So far, analysis of spray paints has been mainly limited to the forensic field. Micro-infrared reflectance spectroscopy (Zieba-Palus 2005), pyrolysis gas chromatography – mass spectrometry (Py/GC-MS) (Milczarek 2009), a combination of optical microscopy, Fourier transform infrared (FT-IR) spectroscopy and X-ray fluorescence (Govaert 2004, Govaert 2001), or Raman and FT-IR spectroscopy (Buzzini 2004) have been employed. In a few studies on laser cleaning techniques preliminary characterization of the graffiti materials has been reported, focusing on the main binders and inorganic pigments/fillers (Rivas 2012, van der Werf 2007). Some other studies specifically concern the characterisation of vehicle paints (Zieba-Palus 2006, Zieba Palus 2011, Sheng-Hsiung 2012, Plage 2008), whereas investigation of modern paints in general is much more diffused.

FT-IR spectroscopy is one of the most powerful techniques for paint characterisation. Although it might be unreliable for the detection of minor components, it is rather successful in determining the type of paint by identifying the main resins, pigments and fillers (Schaning 2009, Zieba-Palus 2005, Milczarek 2009, Cappitelli 2006, Domenech- Carbò 2011). In fact, FT-IR spectroscopy can be efficiently used to fingerprint most synthetic polymer systems, but generally does not provide information on small differences in the chemical structure of the monomeric units.

Moreover, FT-IR spectroscopy has the potential to identify organic pigments in modern paints, but since the spectra usually contain intense bands related to the binding medium components and, to some degree, also to inorganic pigments/extenders, identification is often difficult.

As already mentioned, modern paints are complex chemical systems and, consequently, their characterisation largely benefits from a separation step. By coupling size exclusion chromatography with FT-IR spectroscopy it is possible to get information on the molecular dimensions and chemical composition (Scalarone 2004).

Py/GC-MS is another technique that is frequently applied to the study of modern paint materials. Definitely, this technique may provide information on polymers, dyes, pigments and additives (Ploeger 2008, Chiantore 2003, Learner 2004, Pintus 2011, Bonaduce 2013, Peris-Vicente 2009). It has proven to be a fast method for the identification of organic pigments that yield sufficiently volatile pyrolysis products and thus, unfortunately, this technique has displayed a rather low sensitivity for non-azo organic pigments (Ghelardi 2015, Russell 2011, Sonoda 1999, Rehorek 2007). Since the late 1980s modifications of the pyrolysis process that involve high-temperature chemical reactions other than conventional thermolysis of macromolecules, have been reported. For instance, thermally assisted hydrolysis and methylation (THM) (Cappitelli 2004, Cappitelli 2006, Ploeger 2012, Ploeger 2008) or silylation (Osete-Cortina 2006, Domenech-Carbò 2009) have been used for investigation of modern paints, in particular of synthetic polymers such as alkyds, acrylics and phenolic resins.

Direct temperature resolved mass spectrometry (DTMS) has also been applied to the analysis of modern paints (Boon 2002, Learner 2004). Indeed, DTMS has shown to be successful in the identification of organic pigments in acrylic paints used by the American artist Sam Francis (Menke 2009).

Commonly used methods for inorganic pigment identification are scanning electron microscopy in combination with energy dispersive X-ray spectroscopy (Domenech-Carbò 2001) as well as X-ray diffraction (Hochleitner 2003). However, the most widely used method for the identification of both inorganic and organic pigments and dyes is Raman spectroscopy (Colombini 2010, Clark 2001, Scherrer 2009, Schulte 2008, Brosseau 2009, Vandenabeele 2000). For forensic purposes this

technique has been applied with the aim to differentiate paint samples of similar colour and shade (Zieba-Palus 2011, Zieba-Palus 2006, Buzzini 2004, Buzzini 2006), also by recurring to chemometric methods (Muehlethaler 2011). Some difficulties may, however, arise when strong fluorescence is produced by some paint components, which may overwhelm weak Raman scattering peaks (Zieba-Palus 2011). In order to minimise this phenomenon, FT-Raman spectroscopy, which uses near infrared excitation, may be applied (Kupstov 1994, Ellis 1990). Other authors propose the usage of surface-enhanced Raman spectroscopy that allows to obtain an enhanced Raman signal and substantial quenching of fluorescence through the use of noble metal substrates (Buzzini 2004, Brosseau 2009).

The aim of this study is to determine the chemical composition of a large variety (N.45) of spray paints that are commercially available in Italy and Spain and are commonly used for the realisation of graffiti and decoration purposes. Literature studies are few and have mainly been focused on the analysis of spray paints in the forensic field assessing the discrimination potential of the techniques that were employed. Chemical characterization has been generally limited to the determination of the main binders.

In this study a multi-technique approach was used in order to fully characterise the spray paint formulations (main and minor binders, plasticisers, inorganic and organic pigments, fillers and other additives). Each sample was first examined with FT-IR spectroscopy as a preliminary step to obtain indications on the main binder, which could then be confirmed and detailed using Py/GC-MS. Some pigments and extenders could be efficiently identified by examination of FT-IR spectra and detection of characteristic pyrolysis products, but a thorough characterisation of organic and inorganic pigments, extenders and fillers was successfully accomplished with  $\mu$ -Raman spectroscopy.

## **2. Experimental**

### **2.1 Materials**

A selection of n. 45 spray paints of various brands and manufacturers was analysed. Eleven spray paints were purchased in Spain (S\_1-S\_11), the other ones in Italy (**Errore. L'origine riferimento non è stata trovata.**). All spray paints are commonly used for the realization of graffiti or for decoration purposes, with the exception of two samples (S\_44-S\_45) (*Spraycar*) that are usually employed for the repair of small defects of automotive paints.

The spray paints were applied to glass slides, followed by complete solvent evaporation for about two weeks. Different aliquots of sprayed dry films were sampled and analyzed either after grinding (FTIR) or as such (Py/GC-MS), e  $\mu$ -Raman spectroscopy??? Sul vetrino?

Poly(styrene-co- $\alpha$ -methylstyrene) and tetramethylammonium hydroxide (TMAH) (25% in H<sub>2</sub>O) were purchased from Sigma Aldrich (Milan, Italy), whereas copper phthalocyanines (CuPc) reference pigments (Blue Heliogen 23050 (PB15:1), Blue Heliogen 23060 (PB15:3), Blue Heliogen 23070 (PB15:6), Green Heliogen 23000 (PG7), Green Heliogen 23010 (PG36)) were obtained from Kremer Pigmente GmbH & Co (Aichstetten, Germany).

## 2.2 Methods

### *FTIR spectroscopy*

FTIR spectroscopy was carried out with a BIORAD FTS6000 spectrophotometer, equipped with a KBr beamsplitter and DTGS detector. Pellets for absorbance analyses were prepared by grinding with potassium bromide (*ca.* 2 mg of sample/200 mg of KBr). Spectra were acquired in the 4000 and 400 cm<sup>-1</sup> range at a resolution of 4 cm<sup>-1</sup> and by summing 64 scans.

### *Py/GC-MS*

The pyrolysis experiments were carried out with a microfurnace pyrolyser injection system Pyrojector II (SGE, USA). Small amounts (< 0.1 mg) of sample were inserted into a quartz tube (4 cm × 0.53 mm) which was then introduced into the microfurnace operating at a temperature of 500 °C and at a pressure of 18.0 psi. The pyrolysis chamber was directly connected to the injection port (T=280 °C) of a Perkin Elmer Clarus 680 chromatograph coupled with a Perkin Elmer Clarus SQ8T single quadrupole mass spectrometer. The MS transfer line temperature was 260 °C, and the MS ion source temperature was kept at 250°C. The mass spectrometer was operating in the EI positive mode (70 eV) with a scan range of 45–400 m/z. For the gas chromatographic separation, a 5% diphenyl–95% dimethyl polysiloxane column (Perkin Elmer Elite-5MS; 30 m × 0.25 mm i.d., 0.25 μm film thickness) was used. The injector was operated in split mode, the split ratio being dependent on the sample size. The column oven temperature program was 40 °C (4 min hold) to 250 °C at a heating rate of 15 °C/min (7 min hold). The carrier gas (He) was used in constant pressure mode at 13.0 psi. Identification of compounds was performed with the NIST11 MS library search and comparison with literature data.

In order to disclose all components of the alkyd resins, if phthalic anhydride was revealed, the spray paint was also analyzed with THM-GC-MS, in order to allow for hydrolysis and methylation and correct elution of more polar molecules such as polyols and fatty acids. To this purpose 10 μl of tetramethylammonium hydroxide 2.5% (w/w) in methanol was grinded with the sample before introduction into the quartz tube.

#### *μ-Raman spectroscopy*

The micro-Raman spectra were recorded with an Xplora (Horiba JobinYvon) instrument equipped with three lasers ( $\lambda_0=532, 638$  and  $785$  nm). Sample irradiation was accomplished using the 50× and 100× microscope objectives of an Olympus BX41 microscope. The exposure time, beam power and accumulations were selected to get sufficiently informative spectra. The laser spot size was adjusted between 1 and 3 μm. Raman scattering was filtered by a double holographic notch filter system and



collected by an air-cooled CCD detector. The wavelength scale was calibrated using a Si(111) standard ( $520.5\text{ cm}^{-1}$ ).

For the analysis of the white spray paint samples a green laser ( $\lambda_0 = 532\text{ nm}$ ) was used, whereas for the red, yellow, brown and black samples a red laser source ( $\lambda_0 = 638\text{ nm}$ ) was employed. All blue and green spray paints were investigated by using the  $\lambda_0 = 785\text{ nm}$  laser in order to compare with literature data (see below). This laser was also used in order to minimise the fluorescence phenomena which were observed for some samples.

For the identification of the blue copper phthalocyanine (CuPc) polymorphs special care was taken to use a constant setting for the analysis of the dry reference pigments and the spray paint samples. In particular, all spectra were acquired by using a diode laser with a wavelength of 785 nm. The laser power was reduced at 10% ( $\sim 4\text{ mW}$ ). Three spectra from different pigment grains were recorded in the spectral range of  $80\text{--}2000\text{ cm}^{-1}$  by using a  $50\times$  objective with an exposure time of 4s and 30 accumulations. The averaged intensity ratios were calculated from the baseline-corrected spectra and were not normalised.

### **3. Results and discussion**

#### **3.1 Binders**

The results of the binder composition analysis will be separately discussed for FTIR spectroscopy and Py/GC-MS. All compositional data are resumed in Tables 2-4.

##### **3.1.1 FTIR spectroscopy**

FT-IR spectroscopy was used for a first 'screening' of the main binders, pigments and extenders present in the spray paints. On the basis of these results the samples could be classified into three

groups according to the type of main binder: alkyd resins (Table 2), styrene-acrylic resins (Table 3) and styrene-based resins (Table 4).

### *Alkyd resins*

Alkyd resins are made by condensation polymerisation of polyols - with at least three hydroxyl groups - and polybasic acids. The most frequently used polyols in alkyd formulations are glycerol and pentaerythritol, whereas the most common polybasic acid is ortho-phthalic acid, but iso-phthalic, terephthalic, maleic and fumaric acids may also be employed (Learner 2004). Terephthalic acid is less expensive but tends to crystallize forming hazy resins and generating film defects (Ploeger 2008). When alkyd resins are used as paint binders, they are usually modified with fatty acids, either derived from oil or from synthesis, to make them sufficiently flexible. If siccative oils are added, the nature of the fatty acids determines the final drying characteristics of the paint material, since drying is obtained through auto-oxidation reactions after solvent evaporation.

The spray paints of the alkyd group that were investigated in this work were found to contain: i) alkyd resin and ii) alkyd resin modified with nitrocellulose. Modification with nitrocellulose increases the gloss, adhesion and hardness of the paint film. Minor quantities of styrene may also be present (Table 2).

**In Errore. L'origine riferimento non è stata trovata.** the FTIR spectrum of a blue spray paint (S\_4) (*Dupli-Color*) based on alkyd resin modified with nitrocellulose and styrene is reported. In this spectrum absorptions relative to an ortho-phthalic alkyd resin can be found. Peaks are present at 2955, 2925 and 2855  $\text{cm}^{-1}$  (C-H stretching vibrations), but the spectrum is dominated by a prominent absorption band of the benzoate ester bond stretching at 1726  $\text{cm}^{-1}$ . In the fingerprint region a characteristic peak at 1270  $\text{cm}^{-1}$  (here present as a shoulder of the intense 1278  $\text{cm}^{-1}$  absorption), related to the C(=O)-O asymmetric stretching vibration, and one at 1070  $\text{cm}^{-1}$  due to the C-C-O asymmetric stretching vibration of the aromatic ester group can be observed. The modification with

styrene can be easily recognized from the presence of aromatic C-H out-of-plane bending vibrations with strong absorptions at 701 and 744  $\text{cm}^{-1}$ . Additional peaks are observed at 3030  $\text{cm}^{-1}$  (C-H stretching), 1454 and 1495  $\text{cm}^{-1}$  (aromatic ring breathing).

In the spectrum of Figure 1 a strong  $\text{NO}_2$  stretching peak can be found at 1655  $\text{cm}^{-1}$ ; other characteristic peaks of the cellulose nitrate component are detected at 1278, 1070 and 840  $\text{cm}^{-1}$ , respectively due to the C-O, C-C and C-N stretching modes.

### *Styrene-acrylic resins*

Various spray paints that were analysed in this study show the main absorptions of an acrylic binder, often in combination with styrene (Sty) or with Sty copolymerized with  $\alpha$ -methyl-styrene ( $\alpha$ MSty). In many of these samples the acrylic part can be ascribed to n-butylmethacrylate (nBMA) and methylmethacrylate (MMA). In Figure 2 the spectrum of a red spray paint (S\_29) (*Arexons*) containing a nBMA-MMA-Sty- $\alpha$ MSty copolymer is shown. A strong doublet at 2955 and 2930  $\text{cm}^{-1}$  with a shoulder at 2876  $\text{cm}^{-1}$ , corresponding to the C-H stretching vibrations of the acrylic groups, can be observed, whereas the strongest peak at ca. 1733  $\text{cm}^{-1}$  can be attributed to the carbonyl stretching (C=O). The latter peak does not allow for discrimination of the various types of acrylic resins nor for a distinction from alkyd resins. The peak at 1460  $\text{cm}^{-1}$  is due to the C-H bending of the acrylic fraction, whereas the C-O and C-C stretching peaks of nBMA and MMA are visible at 1150, 1062 and 966  $\text{cm}^{-1}$ .

As already mentioned, many of the acrylic resin-based spray paints show FT-IR spectra with characteristic absorptions of styrene, as illustrated by the spectrum reported in Figure 2: two very weak bands at 3030 and 3064  $\text{cm}^{-1}$  due to the C-H stretching vibrations; absorptions at 1450, 1495 and 1610  $\text{cm}^{-1}$ , which can be ascribed to the aromatic skeletal ring breathing vibrations, and aromatic C-H out-of-plane bending modes at 702 and 761  $\text{cm}^{-1}$ . When a weak peak is present at 3083  $\text{cm}^{-1}$  and a more intense peak at 1599  $\text{cm}^{-1}$  can be detected, the occurrence of a copolymer of styrene and  $\alpha$ -methyl-styrene was suggested.

### *Styrene-based resins*

For the metal spray paints that were examined in this study the main FT-IR signals are due to the presence of a Sty- $\alpha$ MSty copolymer. Indeed, as can be clearly observed in Figure 3, the spectrum of the gold metal spray S\_25 (*Arexons*) completely matches that of a reference material of poly(styrene- $\alpha$ -methyl-styrene). The aromatic C-H stretching peaks at 3083, 3063 and 3030  $\text{cm}^{-1}$  are evident together with the non-aromatic C-H stretching bands at 2959 (-CH<sub>3</sub>), 2924 (-CH<sub>2</sub>) and 2870 (-CH<sub>3</sub>)  $\text{cm}^{-1}$ . Furthermore, sharp intense peaks corresponding to the aromatic ring breathing (1599, 1495 and 1450  $\text{cm}^{-1}$ ), an absorption at 1030  $\text{cm}^{-1}$  and two C-H out-of-plane bending peaks (760 and 702  $\text{cm}^{-1}$ ) are clearly visible and coincide with those of the reference spectrum. Overtone and combination bands for mono-substituted aromatic ring systems were observed in the 2000–1700  $\text{cm}^{-1}$  region.

### **3.1.2 Py/GC-MS**

The Py/GC-MS results allowed not only to confirm the ‘main binder’ classification of the spray paints based on the FT-IR spectroscopy data, but also to divide these groups into subgroups taking into account the minor binders (Tables 2-4).

### *Alkyd resins*

The majority of the alkyd resin spray paints analysed in this study contains ortho-phthalic acid. During pyrolysis phthalic anhydride ( $m/z$  148) is typically produced by cleavage of the C-O bond. This characteristic product was detected in the *Dupli Color*, *Fly Color*, *Montana Colors*, *Tecnoral* and *Spray car* spray paints. In some cases a small amount of benzoic acid ( $m/z$  122) was also observed, which is most likely formed by decarboxylation of phthalic acid. This process becomes prevalent for alkyd resins that are based on iso-phthalic acid.

In the pyrograms of the alkyd spray paints low amounts of acrylic monomers, styrene and various pyrolysis products of poly(vinylphenylketone) (PVPK) could also be detected. The main characteristic pyrolysis fragments of PVPK, *i.e.*, benzaldehyde ( $m/z$  106), 1-phenyl-ethanone ( $m/z$  120), 1-phenyl-1-propanone ( $m/z$  134), 2-methyl-1-phenyl-2-propenone ( $m/z$  146), and benzophenone ( $m/z$  182) were found (Van der Werf 2009). PVPK is known to be a component of clear and pigmented coatings and inks, which may be added in order to improve the adhesion, gloss and pigment loading. In the *Fly Color* spray paints a relatively high quantity of benzophenone was detected. This compound may be added to paint formulations as photoinitiator, UV blocker etc.

Py/GC-MS enabled to better elucidate the complex composition of the alkyd formulations. Various types of additives could be successfully detected, such as the following plasticisers: di-isobutyl phthalate (DIBP), diisooctyladipate (DIOA), dibutyl itaconate (DITA), ethyl citrate (Citroflex) and the 2-ethylhexyl diester of hexanedioic acid (ADIPOL). In Figure 4 the pyrogram of a red spray paint *Dupli Color* (sample S\_3) is shown. All identified compounds are listed in Table 5. A strong peak attributed to phthalic anhydride can be observed at a retention time (RT) of 12.10 min. Other pyrolysis products are related to the presence of an acrylic resin, *i.e.*, 2EHA and styrene. Moreover, the red azo pigment PR170 could be easily recognised on the basis of its characteristic pyrolysis products: 2-naphthol, 2-ethoxy-benzenamine, ethoxybenzene and 2-ethoxy-phenylisocyanate (see 3.2 Pigments, fillers and extenders).

As specified in the experimental section, when phthalic anhydride was found, the spray paint sample was also analysed with on-line thermally assisted hydrolysis methylation using TMAH. Addition of TMAH allows the detection of the methyl esters of ortho-phthalic and tere-phthalic acid. Decarboxylation and methylation of phthalic acid may explain the presence of the methyl ester of benzoic acid. The pyrograms of all the alkyd resin spray paints, revealed the presence of methylated short and medium chain monocarboxylic and dicarboxylic acids such as succinic acid (C4), glutaric acid (C5), adipic acid (C6), caprylic acid (C8), suberic acid (C8), azelaic acid (C9), lauric acid (C12), myristic acid (C14), palmitic acid (C16), and stearic acid (C18); branched short chain acids were also present. The trimethyl ether of pentaeritritol was revealed. This type of polyol had been used in all

alkyd formulations examined in this study.

### *Styrene-acrylic resins*

The pyrograms of the second main group of spray paints are characterised by intense peaks of acrylic compounds and in many cases styrene was detected as well. According to the literature, the most commonly used acrylic co-polymers for paint formulations are the following: poly (ethylacrylate-methylmethacrylate) (EA-MMA), poly(nBA-MMA), and poly(2-ethylhexylacrylate-methylmethacrylate) (2EHA-MMA), often present as copolymers with styrene (Pintus 2012). In fact, the combination of different acrylic monomers determines the glass transition temperature ( $T_g$ ), which should be high enough to prevent the dried film from becoming tacky and yet sufficiently low to avoid cracking due to excessive brittleness. The value of  $T_g$  decreases with the length of the side chain, reaching a minimum for p(2EHA). However, it is important to consider that the  $T_g$  value also depends on other factors such as the molecular weight, degree of crystallinity, cross-linking, etc.

The pyrograms of the spray paints that were examined in this study present either one type of acrylic monomer, *i.e.*, 2EHA, nBMA or MMA, or a combination of two or more acrylic monomers such as 2EHA-MMA-nBA or n/i-BMA-MMA, in addition to styrene or Sty- $\alpha$ MSty.

Methacrylate-based polymers produce rather simple pyrograms, since pyrolysis generates a typical “unzipping” depolymerization mechanism leading to the formation of the constituent monomers.

In all acrylic spray paints nBMA was found with the exception of the red spray paint S\_9 where iBMA was used together with MMA. When nBMA was identified as the major pyrolysis product, traces of iBMA could also be detected.

Differently, the pyrograms of acrylate-based resins usually show quite small monomer peaks whose mass spectra are characterised by a base peak at  $m/z$  55. In addition, several other compounds due to the pyrolytic fragmentation of the monomer are usually observed. For instance, nBA-based polymers may generate 2-butene, 2-buten-1-ol, 2-methyl-2-butenal, and n-butyl acrylate, whereas 2-EHA may produce pyrolysis products of higher intensity than the monomer itself which may even be absent.

The acrylic spray paints were found to contain different minor binders, such as alkyd resin and PVPK or vinyl toluene (VT). Only in a few samples plasticizers, *e.g.*, DIOA, DIBP, Adipol, Citroflex and camphene, were identified.

As an example, the pyrogram of the yellow styrene-acrylic spray paint S\_39 (*Capec*) is reported in Figure 5. The identified compounds are listed in Table 7. The main peaks could be ascribed to MMA, nBMA styrene and to VT. Moreover, various characteristic products due to the pyrolysis of the yellow pigment PY74 were found (see 3.2 Pigments, fillers and extenders).

### *Styrene-based resins*

As was already suggested by the FT-IR spectra, the Py/GC-MS data indicate that a few spray paints, in particular the very tough 'metallic' spray paints, contain a main binder composed of poly(Sty- $\alpha$ MSty). In fact, although  $\alpha$ -methyl-styrene is a pyrolysis product of polystyrene (Tsuge 2011), when it is present in large amounts the occurrence of a  $\alpha$ -methyl-styrene monomer can be reasonably hypothesised. In addition, a DIBP plasticizer and small amounts of acrylic and alkyd resin were found in this type of spray paints.

## **3.2 Pigments, fillers and extenders**

All identified pigments, fillers and extenders are reported in Table 7.

### **3.2.1 FT/IR spectroscopy**

Some pigments and materials that were used as fillers and/or extenders were also identified with FTIR spectroscopy.

The mono-azo aceto-acetyl yellow pigment PY74 could be easily recognised from the characteristic absorptions at 1672, 1518, 1335, 1287, 1221, 1177, 1085 and 1019  $\text{cm}^{-1}$  in samples S\_14, S\_29, S\_39

(Learner 2004). The mono-azo naphthol AS red pigment PR112 was identified in sample S\_13 on the basis of weak absorbance peaks at 1675, 1599, 1559 and 1018  $\text{cm}^{-1}$ , whereas the red naphthol AS PR170 was found in sample S\_38 due to the presence of peaks at 1654, 1610, 1555, 1391, 1266 and 1018  $\text{cm}^{-1}$  (Learner 2004). Furthermore, in the red *Arexons* spray paint (S\_29) the occurrence of the orange mono-azo benzimidazolone pigment PO36 could be established from the peaks at 3370, 1697, 1657, 1565, 1490, 1138, 1189 and 1004  $\text{cm}^{-1}$ .

The white titanium pigment rutile (PW6), which was found in many samples, could be identified from the very broad absorption in the low wavenumber range of the spectrum (between 500 and 900  $\text{cm}^{-1}$ ).

Moreover, FT-IR spectroscopy allowed for the identification of chalk, gypsum and talc used as extenders. Calcium carbonate (PW18) was found in many spray paints, especially in the *Arexons* types and could be identified on the basis of a broad absorption band between 1400 and 1500  $\text{cm}^{-1}$  with a maximum at 1414  $\text{cm}^{-1}$  due to the asymmetric stretching band of  $\text{CO}_3^{2-}$ . A sharp peak at 877  $\text{cm}^{-1}$  (out-of-plane bending) and a less intense peak at 713  $\text{cm}^{-1}$  (in-plane bending) were also present. Talc and gypsum could also be found, although less frequently. Talc (PW26), a hydrous magnesium silicate mineral ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), was recognized in a grey *Molotow* and in a black *Montana Colors* spray paints showing two sharp peaks, one more intense at 1015  $\text{cm}^{-1}$  and another one at 669  $\text{cm}^{-1}$ . This mineral is used in paint formulations as an extender and filler in order to improve the suspension of solids and the adhesion of the liquid paint to a vertical surface without sagging; it may also be added for whitening and brightening of the paint. Gypsum was recognized in a few spray paints by the presence of a strong sharp peak at 1129  $\text{cm}^{-1}$  and two less intense peaks at 667 and 1618  $\text{cm}^{-1}$ .

### 3.2.2 Py/GC-MS

The Py/GC-MS analyses allowed to identify various azo and polycyclic pigments. Several studies report on Py/GC-MS of different classes of synthetic pigments and were used for comparison



(Learner 2001, Learner 2004, Sonoda 1999, Russell 2011, Rehorek 2007, Chiantore 2003, Ghelardi 2015).

The azo-pigments that were encountered in the spray paints belong to the monoazo (acetoacetic arylide and naphthol AS) and disazo (pyrazolone) pigments.

Azo-pigments are prepared by the coupling of a diazo- and an electron-rich aromatic compound. Under pyrolytic conditions the azo groups are rather labile and degrade by elimination of molecular nitrogen or reduction to amines. The amide group is also prone to thermal degradation leading to the formation of the amino derivative or rearranging to isocyanate.

In various spray paints the monoazo arylide yellow pigments PY1, PY3 and PY74 were identified. The latter pigment was most frequently found. Arylides are produced by using acetoacetyl arylides as the coupling component, which fragment producing amine and isocyanate. As already reported in literature (Sonoda 1999), the presence of acetylcyanide, 2-methoxy-benzenamine, 1-isocyanate-2-methoxy-benzene, and 2-methoxy-4-nitro-benzenamine could indeed be ascribed to PY74. These compounds were observed in the pyrogram of spray paint S\_39 (*Capec*) reported in Figure 5. For PY1 acetylcyanide, 1-benzene-isocyanate, benzenamine, and 1-nitro-4-methyl benzenamine were identified (Sonoda 1999). The recognition of o-chloro-benzenamine could suggest the presence of PY3 in sample S\_38. Some authors report the formation of other pyrolysis products that may be generated by the coupling and diazo components of this pigment; in particular o-chloro-cyanobenzene (Russell 2011, Sonoda 1999) and 1-nitro-3-chloro-benzene (Scalarone 2004) could be detected.

Naphthol AS pigments are prepared by combining 2-hydroxy-3-naphthoic acid and N-arylamide (coupling component). Pyrolysis of the PR170 coupling component yields the following products: 2-naphthol, 2-ethoxy-benzenamine, and 2-ethoxy-phenylisocyanate (Russell 2011, Sonoda 1999). Ethoxybenzene could be detected as well. The formation of this compound has not been reported before; its presence might be due to fragmentation of 2-ethoxy-benzenamine. The pyrogram of the red spray paint S\_3 (*Dupli-Color*) (Figure 4, Table 6) shows several peaks which can be assigned to these pyrolysis products.

In sample S\_18 3,3'-dichloro-1,1'-biphenyl was detected. This compound is most likely related to the presence of a pyrazolone pigment, but cannot be used to identify a specific compound.

The phthalocyanines constitute a small but rather popular group of blue and green pigments with a macrocyclic structure that can accommodate a metal ion such as copper. The presence of phthalocyanines is generally hypothesised when in the pyrogram 1,2-benzene-dicarbonitrile ( $m/z$  128) is detected. If chloro-benzene is also found, the chlorinated copper phthalocyanine PG7 might be present. Pyrolysis data on phthalocyanines have been reported in some previous studies (Ghelardi 2015, Russell 2011). Russell *et al.* suggest to carry out the pyrolysis experiments at 800°C in order to identify several characteristic halogenated phthalocyanine products (28. Russell 2011). In a preliminary study Py/GC-MS analyses of two green copper phthalocyanine pigments have been performed at various pyrolysis temperatures ( $T_{Py}$ ), ranging from 300° to 800°C, in order to study the composition of the generated products and to establish the most informative temperature [Germinario 2015]. From these results it became clear that  $T_{Py} = 700^{\circ}\text{C}$  and  $T_{Py} = 800^{\circ}\text{C}$  provide the most informative pyrograms, but a pyrolysis temperature of 500°C is already sufficient to fragment the phthalocyanine molecule and to produce some characteristic pyrolysis products, although in small amounts, which enabled the identification of PB15 (samples S\_4, S\_10, S\_19, S\_42) and PG7 (samples S\_5, S\_11, S\_17). PB15 polymorphs, however, cannot be distinguished with Py/GC-MS.

### 3.2.3 Micro-Raman spectroscopy

Micro-Raman microscopy, as expected, was very powerful in the characterisation of inorganic pigments and extenders, as well as of azo pigments and some polycyclic pigments, *i.e.*, phthalocyanines and dioxazines.

*Inorganic pigments, fillers and extenders*

The black spray paints mainly contain carbon black (Pbk7), which could be identified from its sp<sup>2</sup> (*ca.* 1582 cm<sup>-1</sup>) and sp<sup>3</sup> (*ca.* 1330 cm<sup>-1</sup>) Raman bands.

The white pigment rutile (TiO<sub>2</sub>) (PW6) could be recognised on the basis of two characteristic signals observed at 445 and 610 cm<sup>-1</sup> and was found in all white spray paints. In one white (S\_31) and in two metal spray paints (S\_25 and S\_27) lead white (PW1) and gypsum (PW25), used as extender, were detected. Gypsum (PW25) could be recognised from the absorptions at 1007 and 1136 cm<sup>-1</sup>, whereas chalk (PW18) could be efficiently identified on the basis of a peak at 1087 cm<sup>-1</sup>. In sample S\_30 a mixture of carbon black and titanium white was used to obtain the grey colour. Lead chromate (PY34) could be detected in sample S\_21. The characteristic intense absorptions at 360 and 841 cm<sup>-1</sup> could be clearly observed.

### *Azo pigments*

Azo pigments are frequently used in modern paints. The Raman spectra of this class of pigments show some significant differences with respect to other classes of synthetic pigments, especially in the 1700-1100 cm<sup>-1</sup> region. The bands of this region may be ascribed to C-H deformation, aromatic C-C, C=C, C-C, N=N and C-N stretching vibrations, whereas the rather weak absorptions in the 1000-100 cm<sup>-1</sup> region mainly correspond to skeletal vibrations and ring deformations (Vandenabeele 2000). Some of the spectral features are not specific for a particular pigment, but are rather characteristic of this pigment class. For example, the intense Raman feature between 1380 and 1450 cm<sup>-1</sup> is due to the azo N=N symmetric stretching vibrations of the diazo molecules and a band at *ca.* 1490 cm<sup>-1</sup> can be associated with the azobenzene ring vibration. Other bands, instead, are characteristic of specific subclasses and are rather useful for identification: some azo pigments may present C=O and amide bands together with substituent-specific bands, such as those for NO<sub>2</sub>. Moreover, the C-N symmetric stretching (1200-1130 cm<sup>-1</sup>) and C-N symmetric bending (1200-1160 cm<sup>-1</sup>) bands can shift and change their intensity depending on various factors (neighbouring groups, conjugation effect, H-bonding, molecular tautomerism, and substituents on the conjugated benzene).

In the spray paints that were analysed in this study pigments belonging to various subclasses of monoazo pigments (naphthol AS, benzimidazolone, aceto acetyl) and disazo pigments (diarylide and pyrazolone) were identified.

The monoazo acetoacetyl yellow pigment PY74 was found in many spray paints (S\_13, S\_14, S\_21, S\_28, S\_39 and S\_43), not only in the yellow ones, but also in combination with other pigments in differently coloured samples. The spectra of the acetoacetyl sub class display a very intense peak between 1339-1324  $\text{cm}^{-1}$  and two weak bands at 1668 and 948  $\text{cm}^{-1}$ . The PY74 pigment can be easily identified since the spectrum shows a very intense peak at 1329  $\text{cm}^{-1}$  and a band at 1352  $\text{cm}^{-1}$ . In Figure 6 the micro-Raman spectrum of PY74 as identified in sample S\_14 is reported.

In this study the naphthol AS pigment PR170 could be successfully identified in several samples. Characteristic bands of the naphthol AS pigments can be found around 1365  $\text{cm}^{-1}$ , 965  $\text{cm}^{-1}$  (benzylamide), and 1606  $\text{cm}^{-1}$  (benzene quadrant stretching). The PR170 may be identified on the basis of the medium intensity bands at 1515, 1168 and 421  $\text{cm}^{-1}$ , which are specific for this pigment (Sherrer 2009). As an example, the spectrum of PR170 detected in spray paint S\_3 is shown in Figure 7.

The benzimidazolone pigments PO36 and PO62 were found, respectively, in a red and orange spray paints (S\_29 and S\_34). These pigments show rich Raman spectra with several bands at ca. 1600  $\text{cm}^{-1}$ , attributed to aromatic ring vibrations; for PO36 a very intense band at 1487  $\text{cm}^{-1}$  due to the azobenzene ring (10. Colombini 2010), the antisymmetric (1245  $\text{cm}^{-1}$ ) and symmetric (1448  $\text{cm}^{-1}$ ) stretching vibrations of the N-C-N group could be observed.

The disazo pigments that were recognised in the spray paints of this study are the diarylide PY83 and pyrazolone PO13 and PO34 pigments. All disazo pigments spectra show a prominent band at ca. 1600  $\text{cm}^{-1}$  (benzene quadrant stretching). Both pyrazolone pigments display in addition two medium intensity peaks at 1329 and 1275  $\text{cm}^{-1}$ , and a weak band at 1290  $\text{cm}^{-1}$ , which can be respectively attributed to aromatic ring vibrations, C-C stretching and C-H bending vibrations (Scherrer 2009) and to the C-C bridge between the phenyl groups. In Figure 8 the Raman spectrum of PO34 as present in spray paint S\_18 is given.

All diarylide pigments show a very strong peak at  $1394\text{ cm}^{-1}$ . PY83 can be, however, unambiguously identified on the basis of an additional strong peak at  $1254\text{ cm}^{-1}$  and two medium intensity peaks, respectively at  $1334$  and  $264\text{ cm}^{-1}$ .

### *Polycyclic pigments*

The most intense band in the Raman spectra of copper phthalocyanines (CuPc) pigments is observed at  $1520\text{--}1545\text{ cm}^{-1}$  and can be attributed to the pyrrole C=C and aza C-N stretchings. This band, together with those found around  $1335\text{ cm}^{-1}$  (pyrrole C-C stretching) and  $680\text{ cm}^{-1}$  (macrocyclic ring breathing), is considered to be characteristic for this group (54. Lutzenberger 2009).

The different polymorphs of the blue phthalos (PB15:x) might be discerned on the basis of their Raman spectra [Scherrer 2009, Defeyt 2012, Defeyt 2013], although increasing laser power may induce peak shifting towards lower wavenumbers for dry reference pigments [Scherrer 2009, Defeyt 2012] and unambiguous discrimination of CuPc polymorphs in paint samples may be difficult. Chemometrical analysis has been proposed for discrimination (Defeyt 2013, Defeyt 2014). Taking into account these difficulties, in this study Raman spectra were recorded for dry reference pigments (PB15:1, PB15:3, PB15:6), taking care to verify any visible damage on the laser spot after measurement. The obtained averaged band positions and intensity ratios were comparable with literature data (Scherrer 2009, Defeyt 2012). In particular, the proposed intensity ratio 747:680 (Scherrer 2009) appeared, indeed, to be relevant for the distinction of CuPc polymorphs. Subsequently, for each blue, green and black spray paint sample spectra were acquired in three different points by using the same conditions (see Experimental) and Raman bands and intensity ratios were determined. In this way  $\alpha$ -CuPc and  $\beta$ -CuPc could be successfully identified in the spray paint samples, with the exception of sample S\_17 where overlapping peaks hindered a reliable identification of the phthalocyanine polymorph. It should be emphasised that, regardless of the pigment concentrations and different binders, the Raman spectra of the spray paint samples were very similar to those obtained for the reference pigments. However, in agreement with the literature, in

comparison with the dry reference pigments the spray paint samples exhibit their strongest band at higher wavenumbers (1526-1530  $\text{cm}^{-1}$ ). As already mentioned, this shift is most likely due to an excessive laser excitation of the dry pigments (Scherrer 2009), whereas CuPcs pigments that are embedded in paint systems are probably less sensitive (Defeyt 2012).

The Raman spectra of the green spray paints show, in addition to the characteristic bands of the phthalocyanines reported before, a band at 1082  $\text{cm}^{-1}$ , which could be assigned to aromatic chlorine compounds. Moreover, a strong band at 1503  $\text{cm}^{-1}$  and a medium peak at 1283  $\text{cm}^{-1}$  were found. Comparison with literature data (Lutzenberger 2009, Buzzini 2004) and the spectra which were acquired in this study for two green reference pigments, allowed for the identification of the chlorinated copper phthalocyanine PG7.

The dioxazine pigment PV23 could be unambiguously identified in two blue spray paints (S\_24 and S\_36). Its most prominent Raman bands are a triplet at approximately 1345, 1390 and 1430  $\text{cm}^{-1}$ . The 1390  $\text{cm}^{-1}$  band can be assigned to C=C and C=N in-plane vibrations of the pyrroles as well as to ring vibrations of the alkyl pyrroles, whereas the other two may be ascribed to benzene ring vibrations. The pigment exhibits a unique blue-violet shade of exceptional intensity and is currently employed in a variety of paint formulations.

### 3.3 Discussion

Examination of the binder composition results (Tables 2-4) evidences that most samples contain a main binder based on alkyd or on styrene-acrylic resin. In addition, however, various minor binders and additives were detected, enabling in some cases the discrimination of different brands and/or spray paint typologies of the same brand.

The alkyd resins (Table 2), for instance, exhibit a certain variety: the majority was found to be modified with nitrocellulose and in a few samples significant amounts of styrene could be found as well. Some of these spray paints (*Dupli-Color* and *Fly Color*) also contain 2EHA as minor binder and, in many cases, poly-vinylphenylketone (*Fly-Color* and *Montana Color*) could also be retrieved.

In all but two alkyd resin spray paints plasticisers, such as di-isobutyl phthalate and di-isooctyladipate, were identified. The *Tecnoral* and *Spraycar* spray paints are characterized by big amounts of plasticisers, whereas no acrylic monomers or PVPK were revealed.

Concerning the styrene-acrylic spray paints, the majority presents a copolymer of n-butylmethacrylate and methylmethacrylate, alone or in combination with styrene or styrene- $\alpha$ -methyl styrene. Two *Dupli-Color* spray paints, although containing an alkyd-nitro resin, were classified as styrene-acrylic resin types, since their 2EHA content is prevailing. Differently from the alkyd resin types, in the styrene-acrylic ones plasticizers were rarely detected, probably because of the satisfying physical properties. On the contrary, in this type of spray paints extenders such as chalk and gypsum seem to be more abundant.

Few samples, *i.e.*, the metal spray paints, present a rather simple composition being mainly based on a styrene –  $\alpha$ -methyl-styrene copolymer binder.

It should, however, be pointed out that the indications reported on the can labels concerning the binder composition do not always reflect the chemical composition. For instance, “Acryl” spray paints sometimes revealed to contain major amounts of alkyd(-nitro) resin and only in some cases minor quantities of acrylic components.

As to the pigments, the spray paint formulations examined here show an ample selection. Inorganic pigments were found for the white (rutile) and black (carbon black) samples. Organic pigments were recognized to belong to the azo and polycyclic pigments classes. Among these PY74, PR170 and blue CuPc were most frequently identified.

#### **4. Conclusions**

As already evidenced, the chemical characterisation of spray paints, being multi-component systems containing one or more polymeric binders, pigments and additives, requires high resolution and sensitive techniques. Therefore, in this study we proposed the use of FT-IR spectroscopy, Py/GC-MS and micro-Raman spectroscopy as complementary techniques for a complete identification of all components.

The spray paints analysed in this study were chosen among various commercial brands and colours. By combining the results obtained with a multi-technique approach their chemical composition could be successfully determined.

FT-IR spectroscopy and Py/GC-MS permitted to determine the main binders and to classify the samples into three categories: alkyd resins, styrene-acrylic resins and styrene-based resins. The advantage of Py/GC-MS relies in its capability to reveal also minor and trace binders. In order to appreciate the complementary role of these techniques it should be underlined that FT-IR spectroscopy was essential for the detection of nitrocellulose in the alkyd-based spray paints, since Py/GC-MS does not show any peaks relative to cellulose nitrate; on the other hand, Py/GC-MS, was crucial for assessing the co-presence of acrylic and alkyd resins in the same formulation, which is not an easy task to accomplish with FT-IR spectroscopy since the main alkydic absorptions are very similar to the acrylic ones. Moreover, Py/GC-MS was also essential for the unambiguous identification of the acrylic monomers. By using Py-THM-GC-MS it was possible to better investigate the alkyd resin spray paints. In particular, individual fatty acids and polyols could be efficiently detected. Concerning the inorganic components such as extenders and fillers, only by means of FT-IR spectroscopy it was possible to obtain a clear identification.

Finally, as to the analysis of pigments, although FT-IR spectroscopy and Py/GC-MS may provide some information on the presence and nature of these compounds, the most informative technique is micro-Raman spectroscopy. It was possible to recognize inorganic pigments such as carbon black and titanium white, as well as a wide range of synthetic organic pigments of the mono- and disazo, phthalocyanine and dioxazine classes. Generally, FT-IR spectroscopy is poorly informative on pigments since their absorptions are often hidden by the intense bands of the binding medium components. In a few cases unambiguous pigment identification could only be accomplished by means of Py/GC-MS since the recording of micro-Raman spectra was inhibited by fluorescence phenomena. This was the case of the spray paints with fluorescent colours and for the metallic samples.



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## Figure and Table captions

**Fig. 1** FT-IR spectrum of the blue spray paint sample S\_4 (*Dupli-Colour*) based on alkyd resin modified with styrene and nitrocellulose.

**Fig. 2** FT-IR spectrum of the red spray paint S\_29 (*Arexons*) containing a styrene-acrylic resin.

**Fig. 3** FT-IR spectra of the gold metal spray paint S\_25 (*Arexons*) and of poly(Sty- $\alpha$ MeSty).

**Fig. 4** Py/GC-MS trace of the alkyd resin red spray paint S\_3 (*Dupli Colour*).

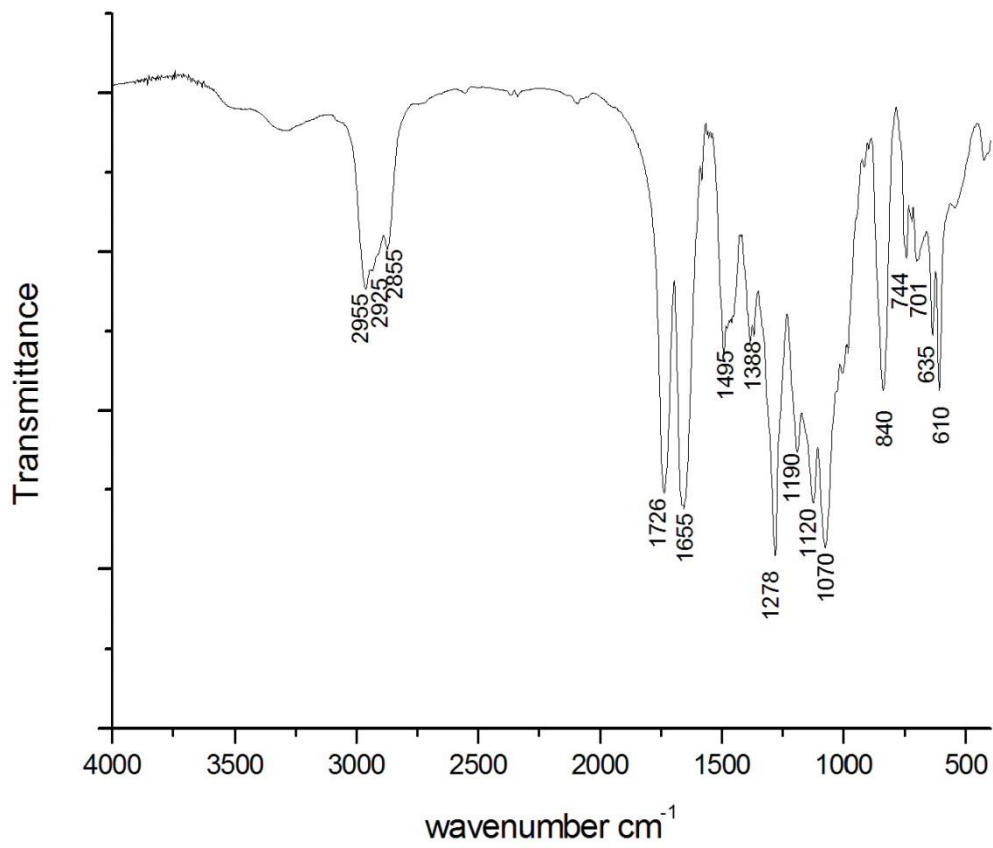
**Fig. 5** Py/GC-MS trace of the acrylic-styrene resin yellow spray paint S\_39 (*Capec*).

**Fig. 6** Micro-Raman spectrum of PY74 as identified in the yellow spray paint S\_14 (*Montana Colours*).  $\lambda_0 = 785$  nm, 20 mW, 1 s exposure time, 100 accumulations

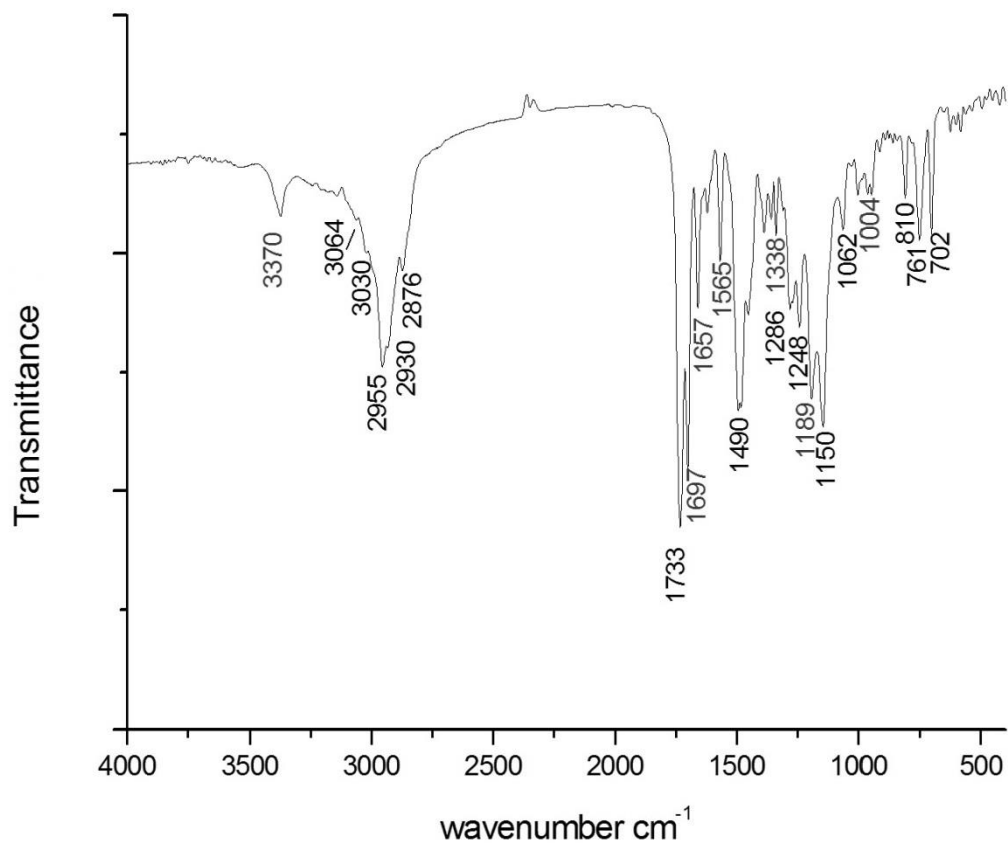
**Fig. 7** Micro-Raman spectrum of PR170 as identified in the red spray paint S\_3 (*Dupli Colour*).  $\lambda_0 = 785$  nm, 20 mW, 1 s exposure time, 100 accumulations

**Fig. 8** Micro-Raman spectrum of PO34 as identified in the orange spray paint S\_18 (*Montana Colours*).  $\lambda_0 = 785$  nm, 20 mW, 1 s exposure time, 100 accumulations

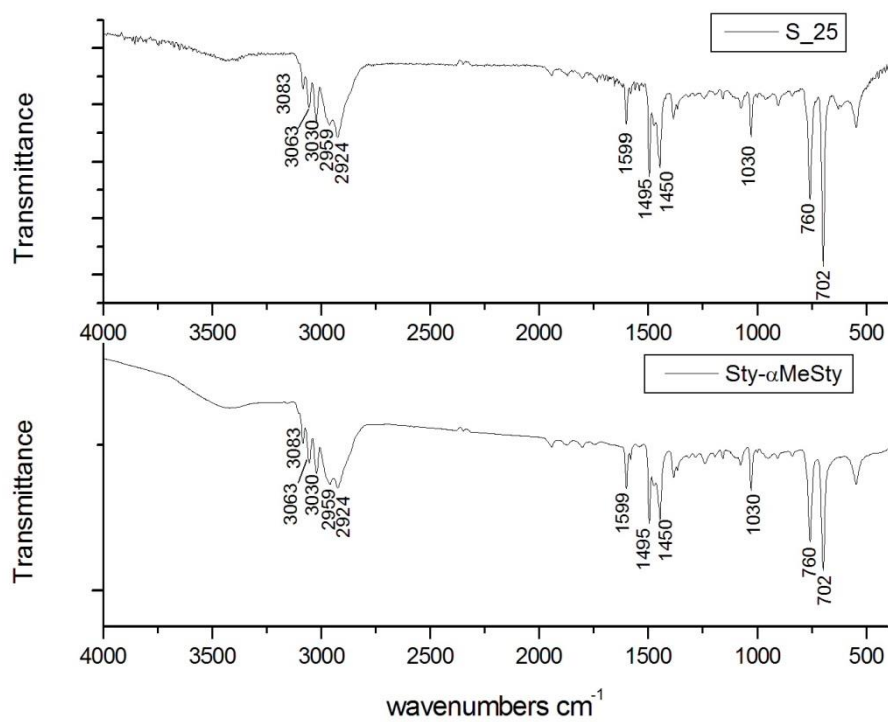




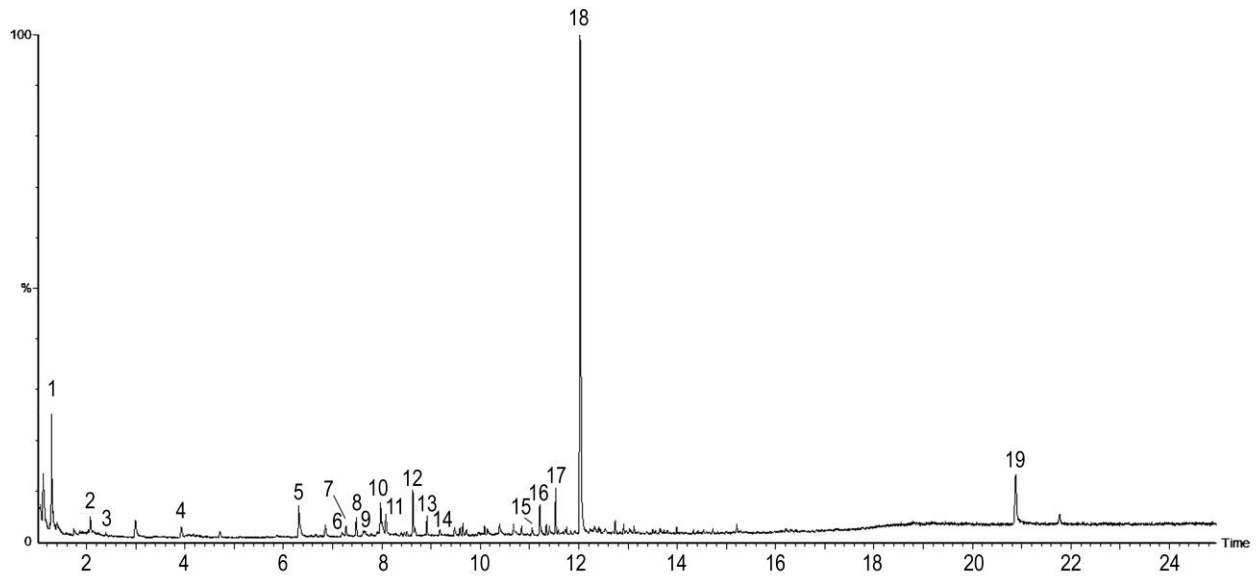
**Fig. 1** FT-IR spectrum of the blue spray paint sample S\_4 based on alkyd resin modified with styrene and nitrocellulose



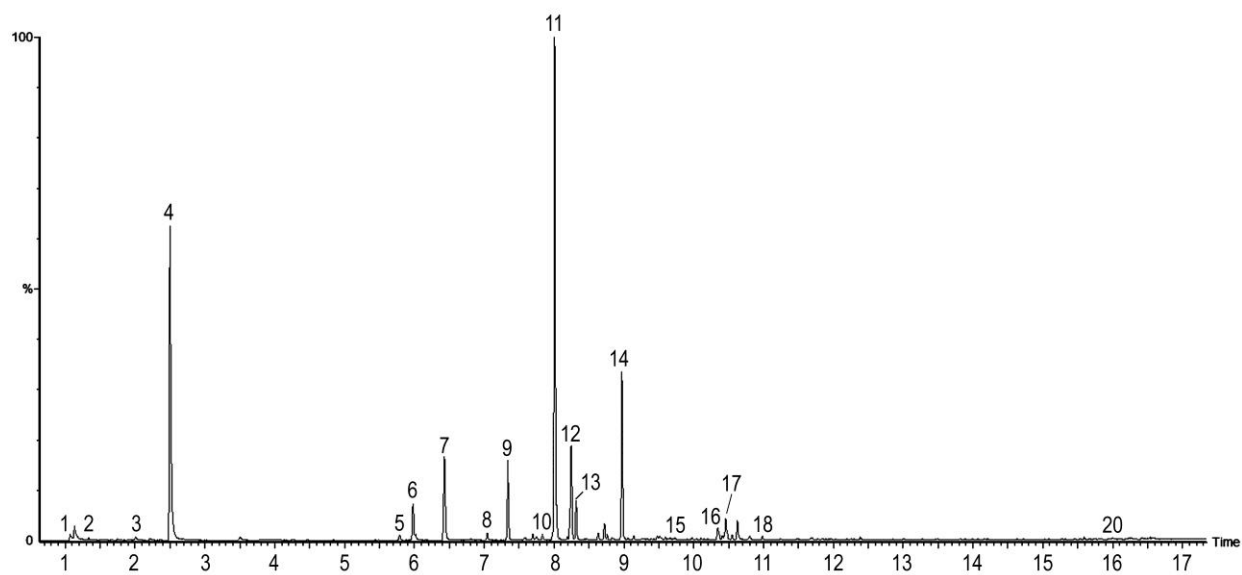
**Fig. 2** FT-IR spectrum of the red spray paint S\_29 (*Arexons*) containing a styrene-acrylic resin



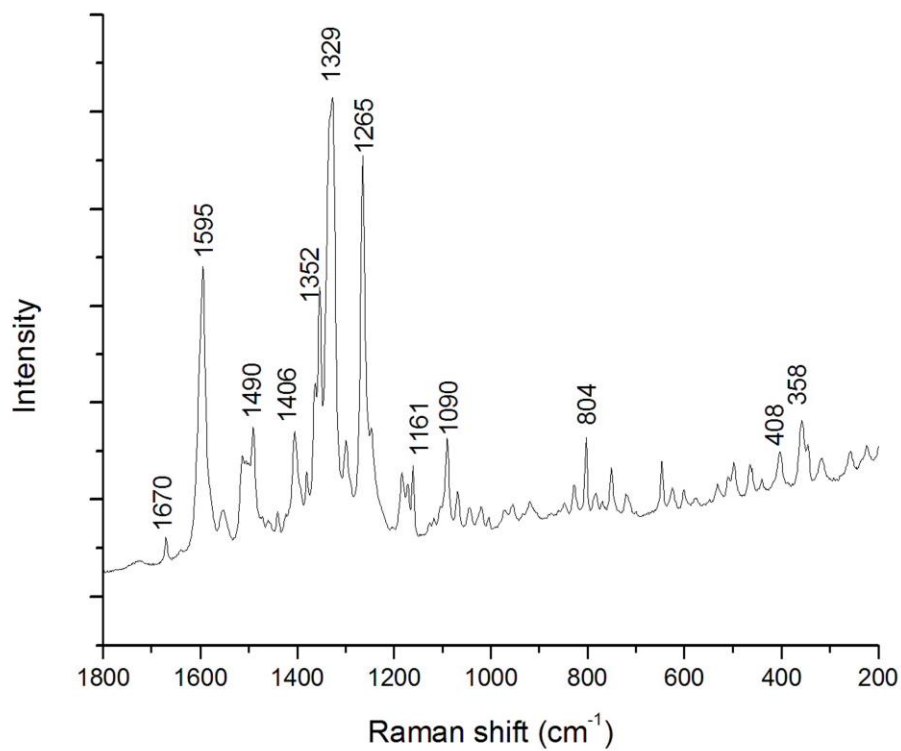
**Figure 3** FT-IR spectra of the gold metal spray paint S\_25 (*Arexons*) and of poly(Sty- $\alpha$ MeSty).



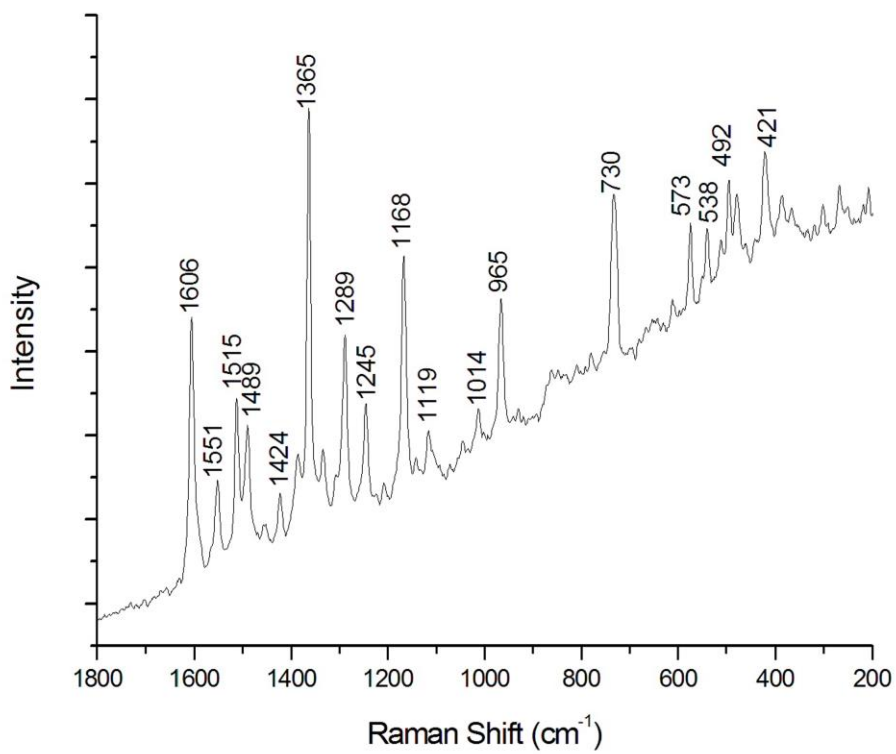
**Fig. 4** Py/GC-MS trace of the alkyd resin red spray paint S\_3 (*Dupli Colour*).



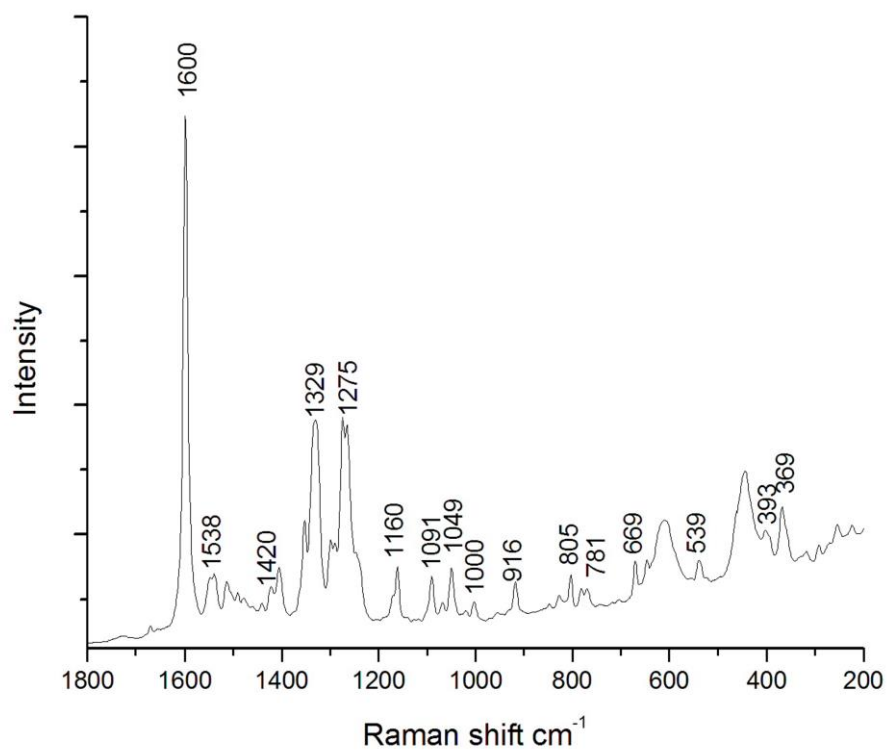
**Fig. 5** Py/GC-MS trace of the acrylic-styrene resin yellow spray paint S\_39 (*Capec*).



**Fig. 6** Micro-Raman spectrum of PY74 as identified in the yellow spray paint S\_14 (*Montana Colours*).  $\lambda_0 = 785$  nm, 20 mW, 1 s exposure time, 100 accumulations



**Fig. 7** Micro-Raman spectrum of PR170 as identified in the red spray paint S\_3 (*Dupli Colour*).  $\lambda_0=785$  nm, 20 mW, 1 s exposure time, 100 accumulations



**Fig. 8** Micro-Raman spectrum of PO34 as identified in the orange spray paint S\_18 (*Montana Colours*).  $\lambda_0 = 785$  nm, 20 mW, 1 s exposure time, 100 accumulations



**Table 1** Samples of spray paint investigated in this study

<b>ID</b>	<b>Manufacturer</b>	<b>Description</b>	<b>Colour</b>
S_1	Dupli-Colour	Acryl (9005)	black
S_2	Dupli-Colour	Acryl (9010)	white
S_3	Dupli-Colour	Acryl (3000)	red
S_4	Dupli-Colour	Acryl (5002)	blue
S_5	Dupli-Colour	Acryl (6002)	green
S_6	Dupli-Colour	AcrylBas (9005)	black
S_7	Fly-Colour	AcrylBas - High gloss (9005)	black
S_8	Fly-Colour	AcrylBas - High gloss (9010)	white
S_9	Fly-Colour	AcrylBas (3000)	red
S_10	Fly-Colour	AcrylBas (5002)	blue
S_11	Fly-Colour	AcrylBas (6000)	green
S_12	Molotow	Belton premium	grey
S_13	Montana colours	94	red
S_14	Montana colours	Pocket	yellow
S_15	Montana colours	Nitro 2G	black
S_16	Montana colours	Hardcore	black
S_17	Montana colours	94	turquoise
S_18	Montana colours	94	orange
S_19	Montana colours	94	blue
S_20	Montana colours	94	white
S_21	Arexons		green
S_22	Arexons	FAI TU colour (2621)	black
S_23	Arexons		bronze (metal)
S_24	Arexons		blue
S_25	Arexons		gold (metal)
S_26	Arexons		pink
S_27	Arexons		silver (metal)
S_28	Arexons	FAI TU colour (2610)	yellow
S_29	Arexons	FAI TU colour (2614)	red
S_30	Arexons		grey
S_31	Arexons	FAI TU colour (2602)	white
S_32	Gioca,Colora e Lavora		sulfur yellow
S_33	Fantastica Ver-O		fluo yellow
S_34	Saratoga	Happy Colour	orange
S_35	Saratoga	Happy Colour metallic 005	gold (metal)
S_36	Keen-Vantage	Vantage (5012)	blue
S_37	Capec	Glossy (9005)	black
S_38	Capec	Glossy (3020)	red
S_39	Capec	Glossy (1003)	yellow

S_40	Capec	Glossy	white
S_41	Capec	COLOURS 104	black
S_42	Velox		black
S_43	Tecnoral	279	yellow
S_44	Spraycar	METALLIC 712	ivory (metal)
S_45	Spraycar	Metallic 501	red

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**Table 2** Composition of the alkyd-resin spray paints

Legend: ADI = Adipol; Alkyd = alkyd resin, 2EHA = 2-ethylhexylacrylate, CIT = Citroflex, DIBP = di-isobutylphthalate, DIOA = di-iso-octyladipate, DIOP = di-isooctylphthalate, DITA = di-isoctylitaconate, Nitro = nitrocellulose, PVPK= poly-vinylphenylketone, Sty = styrene

ID	Manufacturer	Colour	Main binder	Minor binder	Additives
S_1	Dupli-Colour	Black		2EHA	DIOA-DITA
S_2	Dupli-Colour	White		2EHA-Sty	DIOA
S_3	Dupli-Colour	Red		2EHA-Sty	DIOA
S_4	Dupli-Colour	Blue		2EHA-Sty	DIOA
S_7	Fly-Colour	Black		PVPK-Sty	
S_8	Fly-Colour	White	Alkyd-Nitro	PVPK-Sty	DIOA
S_17	Montana colours	Turquoise		PVPK-Sty	DIBP
S_10	Fly-Colour	Blue		PVPK	DIOP
S_11	Fly-Colour	Green		Sty-PVPK	DIOA-CIT-ADI DIBP-
S_43	Tecnoral	Yellow			DIOA
S_44	Spraycar	Ivory (metal)		Sty	DIBP-DIOA
S_45	Spraycar	Red		Sty	DIBP
S_13	Montana colours	Red		PVPK-Sty	DIBP
S_14	Montana colours	Yellow		PVPK-2EHA-Sty	DIBP
S_16	Montana colours	Black		PVPK-Sty	DIBP
S_19	Montana colours	Blue	Alkyd	PVPK-Sty	DIBP
S_18	Montana colours	Orange		PVPK-Sty	DIBP
S_20	Montana colours	White		PVPK-Sty	DIBP
S_12	Molotow	Grey		Sty	DIBP

**Table 3** Composition of the acrylic-styrene resin spray paints

Legend: ADI = Adipol; Alkyd = alkyd resin,  $\alpha$ MSty =  $\alpha$ -methyl-styrene, CAMP = camphene, 2EHA = 2-ethylhexylacrylate, CIT = Citroflex, DIBP = di-isobutylphthalate, DIOA = di-iso-octyladipate, MMA= methylmethacrylate, i/nBMA = i/n-butylmethacrylate, Nitro = nitrocellulose, PVPK= poly-vinylphenylketone, Sty = styrene, VT = vinyltoluene

ID	Manufacturer	Colour	Main binder	Minor binder	Additives
S_24	Arexons	Blue			
S_21	Arexons	Green		VT	
S_28	Arexons	Yellow			
S_29	Arexons	Red	nBMA-MMA/Sty-		
S_30	Arexons	Grey	$\alpha$ MeSty		
S_31	Arexons	White			
S_36	Keen – Vantage	Blue			DIBP
S_40	CAPEC	White		VT	
S_42	VELOX	Black			
S_23	Arexons	Bronze (metal)	nBMA/Sty- $\alpha$ MeSty	VT	
S_26	Arexons	Pink	MMA/Sty- $\alpha$ MeSty		
S_22	Arexons	Black			
S_33	Fantastica Ver-O	Fluorescent yellow			
S_34	Saratoga - Happy Colour	Orange			DIBP
S_37	CAPEC	Black	nBMA-MMA-Sty	VT	
S_38	CAPEC	Red		VT	
S_39	CAPEC	Yellow		VT	
S_41	CAPEC	Black			
S_9	Fly-Colour	Red	MMA-iBMA-Sty	Alkyd-Nitro-PVPK	CAMP-DIOA
S_5	Dupli-Colour	Green		Alkyd-Nitro	DIOA-ADI
S_6	Dupli-Colour	Black	2EHA	Alkyd	DIOA-CIT-ADI
S_15	Montana colours	Black	nBMA-MMA		DIOA

ID	Manufacturer	Colour	Main binder	Minor binder	Additives
S_5	Dupli-Colour	Green	2-EHA	Alkyd	DIOA-ADI
S_6	Dupli-Colour	Black		Alkyd	DIOA-CIT-ADI
S_33	Fantastica V.	Fluo. yellow	nBMA- MMA	VT	

S_9	Fly-Colour	Red	MMA-iBMA	Alkyd-PVPPK	CAMP-DIOA
S_15	Montana colours	Black	nBMA-MMA		DIOA
S_22	Arexons	Black			
S_34	Saratoga	Orange	MMA-nBMA/Sty		DIBP
S_37	CAPEC	Black		VT	
S_38	CAPEC	Red	nBMA-MMA/Sty	VT	
S_39	CAPEC	Yellow		VT	
S_41	CAPEC	Black			
S_23	Arexons	Bronze (metal)	nBMA/Sty- $\alpha$ MeSty	VT	
S_26	Arexons	Pink	$\alpha$ MeSty-Sty/MMA		
S_36	Keen – Vantage	Blue	$\alpha$ MeSty-Sty/MMA-nBMA		DIBP
S_24	Arexons	Blue	Sty- $\alpha$ MeSty/MMA-nBMA		
S_30	Arexons	Grey			
S_21	Arexons	Green		VT	
S_28	Arexons	Yellow	MMA-nBMA/Sty- $\alpha$ MeSty		
S_29	Arexons	Red		VT	
S_31	Arexons	White			
S_40	CAPEC	White	nBMA-MMA/Sty- $\alpha$ MeSty	VT	
S_42	VELOX	Black			

**Table 4** Composition of styrene-based spray paints

Legend:  $\alpha$ MSty =  $\alpha$ -methyl-styrene, Alkyd = alkyd resin, DIBP = di-isobutylphthalate, MMA = methylmethacrylate, nBMA= n-butylmethacrylate, Sty = Styrene

ID	Manufacturer	Colour	Main binder	Minor binder	Additives
S_25	Arexons	Gold (metal)	$\alpha$ MSty-Sty		DIBP
S_27	Arexons	Silver (metal)			DIBP
S_35	Saratoga	Gold (metal)	Sty- $\alpha$ MSty		DIBP
S_32	Gioca, Colora e Lavora	Sulfur yellow		MMA-nBMA-Alkyd	

**Table 5** Pyrolysis products identified in the pyrogram of spray paint S\_3

<b>N.</b>	<b>RT (min)</b>	<b>Assignment</b>	<b>MW</b>
<b>1</b>	1.3	2-methylpropanal	72
<b>2</b>	2.1	2-ethylhexanal	128
<b>3</b>	2.4	methylmethacrylate	100
<b>4</b>	4.0	2-ethyl-1-hexene	112
<b>5</b>	6.4	styrene	104
<b>6</b>	7.2	n-butylacrylate	128
<b>7</b>	7.3	2-methyl-1-hexene	98
<b>8</b>	7.5	2-ethylhexanal	128
<b>9</b>	7.7	benzaldehyde	106
<b>10</b>	8.0	benzonitrile	103
<b>11</b>	8.1	ethoxybenzene	122
<b>12</b>	8.7	2-ethylhexanol	130
<b>14</b>	9.3	1-phenylethanone	120
<b>15</b>	11.1	2-ethylhexylacrylate	184
<b>16</b>	11.3	2-ethoxybenzenamine	137
<b>17</b>	11.6	2-ethoxyphenyl-isocyanate	163
<b>18</b>	12.1	phthalic anhydride	148
<b>19</b>	20.9	di-iso-octyladipate	370

**Table 6** Pyrolysis products identified in the pyrogram of spray paint S\_39

<b>N.</b>	<b>RT (min)</b>	<b>Assignment</b>	<b>MW</b>
1	1.1	2-methylpropene	56
2	1.3	acetyl cyanide	69
3	2.0	1-butanol	74
4	2.4	methylmethacrylate	100
5	5.7	ethylbenzene	106
6	6.0	1,3-dimethylbenzene	106
7	6.4	styrene	104
8	7.0	1-methyl-ethylbenzene	120
9	7.3	i-butylmethacrylate	142
10	7.7	4-methylbenzenamine	107
11	7.9	n-butylmethacrylate	142
12	8.2	1-ethenyl-2-methylbenzene	118
13	8.3	1-propenylbenzene	118
14	8.9	1-propynylbenzene	116
15	9.2	benzene-isocyanate	119
16	10.3	2-methylindene	130
17	10.5	2-methoxybenzenamine	123
18	10.9	1-isocyanato-2-methoxy benzene	149
19	11.4	2-ethyl-1-H-indene	144
20	16.0	2-methoxy-4-nitro-benzenamine	168

**Table 7** Pigments, fillers and extenders identified in the spray paints

Typology/pigment class	Code	C.I.	Spray paints
Carbon black	Pbk7	77261	S_1, S_6, S_7, S_15, S_16, S_22, S_30, S_37, S_41
Rutile	PW6	77891	S_2, S_8, S_20, S_31, S_40
Lead white	PW1	77597	S_21, S_25, S_27, S_31
Chalk	PW18	77220	S_23, S_24, S_27, S_29, S_30, S_32, S_33
Gypsum	PW25	77231	S_25, S_27, S_31
Lead Chromate	PY34	77600	S_21
	PY74	11741	S_13, S_14, S_18, S_21, S_28, S_39, S_43
Monoazo acetoacetyl	PY1	11680	S_5
	PY3	11710	S_38
Disazo- Diarylide	PY83	21108	S_38
	PO13	21110	S_45
Disazo- Pyrazolone	PO34	21115	S_18
Monoazo Benzimidazolone	PO36	11780	S_29, S_34
Monoazo Naphthol AS	PR170	12475	S_3, S_9, S_21, S_38, S_43, S_45
	CuPc	74160	S_17
	$\alpha$ CuPc	74160	S_4, S_10
Phthalocyanines	$\beta$ CuPc	74160	S_19, S_24, S_36, S_42
	PG7	74260	S_5, S_11, S_17