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Discovering the colours of industrial heritage characterisation of paint coatings from the powerplant at the Levada de Tomar

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Abstract

The paint coatings of three energy generators from the 20th-century powerplant at Levada de Tomar, Portugal, were investigated using micro-Raman and micro-X-ray fluorescence spectroscopies and scanning electron microscopy with energy dispersive spectroscopy. This multi-analytical approach was used to identify the colouring agents, thus providing a chronological chromatic pallet and allowing to infer on the use of the three energy generators. Together with traditional pigments like Prussian blue, red iron oxide, and carbon black, pigments used in industrial areas like copper phthalocyanine and toluidine red were identified as colouring agents. Complex paint systems of the oldest equipment (1924) were revealed as well as maintenance procedures of the equipment that worked during a longer time (1944–1990). Powdery carbon black layers, resulting from incomplete hydrocarbon combustion and present between metallic substrates and coating layers, suggested the inexistence of paint coatings replacement after the powerplant shutdown. The identification of magnetite as a corrosion product of iron alloy substrate revealed that corrosion developed after the engine shutdown and not during the operation period. The results obtained highlight the potentialities of scientific-based approach and Raman spectroscopy to the industrial heritage study, an emergent cultural area.

KEYWORDS
conservation, industrial heritage, paint coatings, Raman spectroscopy, SEM-EDS, XRF

1 | INTRODUCTION

Industrial heritage (IH) comprises objects, equipment, and installations that are material evidence of the industry history and technology development.[1] Since the 1970s, the importance of studying and conserving IH objects has been systematically recognised in emerging studies related to its history and conservation.[2,3] However, material analytical-based investigations, which potentially increase the knowledge of IH, are still rather scarce.[4–8] Despite occasional studies employing X-ray fluorescence spectrometry (XRF) and scanning electron

microscopy with energy dispersive spectroscopy (SEM-EDS) for the characterisation of paint coatings[9] and metal alloys of early 20th-century military vehicles[10] and ships,[8,11] the use of other analytical techniques is, to our knowledge, lacking. The application of vibrational spectrometry for the study of IH is yet to be explored. The work by Castro et al.[12] should be emphasised for this area of research. By using FTIR and Raman spectroscopies, the authors approached the manufacturing process of 19th-century wallpapers through the study of pigments and binders used in this industry.

When considering large dimension equipment, such as engines, the analytical characterisation of metals, lubricants, and coatings can contribute to the IH historical and technological knowledge and to IH conservation assessment and can provide evidence on its use.[6,13] Studies of metallic engine components such as valves, tubes, screws, and bolts, to name only a few, by analytical approaches are lacking. Nonetheless, their identification could increase knowledge on the construction of industrial engines, by searching which metal alloys were used according to the components' function. The corrosion study of metal pieces, including the identification of corrosion products, can give information about the preservation of engines, contributing to the definition of conservation procedures, as demonstrated for large ancient vehicles exhibited in Museums.[14] Furthermore, the identification of wear metals in lubricants can provide information on the components use and wear, a current approach used in the monitoring and maintenance of modern industrial engines.[15]

The investigation of paint coatings, due to their dual function of protection and decoration, is of increasing interest. Paint coatings were applied on engines to prevent the corrosion of substrates, mainly of iron and steel, and as a decorative effect, taking advantage of the use of different paint colours. Over an engine lifetime, several maintenance actions would be carried out, including the application of new paint coatings, usually over previous ones. Studies on paint coatings of IH engines use SEM-EDS and optical microscopy for elemental identification and characterisation of the coating system stratigraphy, respectively.[6,9] However, detailed investigation using other analytical techniques, such as Raman spectroscopy, could enable the identification of pigments employed during a certain period providing in that way a chronological chromatic pallet and knowledge on the operation and maintenance of the engine. Based on the potential of the analytical characterisation of IH paint coatings and the scarcity of studies regarding the subject, this study presents an approach to its investigation grounded on the case study of three energy generators from the 20th-century powerplant at the Levada de Tomar, Portugal. In this approach, different paint coatings were analysed to identify the pigments used as colouring agents and to investigate possible changes on the use of those pigments in different engines from different time periods. In order to obtain information on technology techniques and maintenance actions, representative cross-section samples of paint coatings were observed under a stereomicroscope and by SEM-EDS. The elemental composition of the paint coatings was analysed by µXRF. To obtain further information on the structural composition, samples were analysed by µRaman, thus exploiting for the first time the application of this analytical technique to the study of paint coatings of IH engines.

2 | THE GENERATORS OF THE LEVADA DE TOMAR POWERPLANT

The Powerplant at Levada de Tomar, Portugal, founded in 1901 by the company *Jean Bourdain & C.ᵃ*, provided electric street lighting to the city of Tomar. In 1910, the property and the concession of the powerplant were transferred to the company *Sociedade Manuel Mendes Godinho*. In addition to supplying electric light to the city, this company also produced energy to the cereal mill factory *A Portuguesa* established next to the powerplant. During this period, the owners endued the powerplant with new equipment. In 1919, a steam turbine with a boiler was installed, and in 1924, a hydraulic generator with a Francis-type turbine was set-up. A diesel engine was acquired in 1927, and later, in 1944, a hydraulic generator with a propeller-type turbine was installed. Except for the steam turbine, which was destroyed, the other energy generators still exist at the powerplant, although deactivated (Figure 1). The information about the operation periods of the engines and the extent of their use is scant. However, it is known that in the 1950s, the concession for electricity production to urban consumption ended and that in 1996, the powerplant ceased activity.[16]

Table 1 lists the energy generators groups, their manufacturers, year of implementation at the powerplant, constitutive materials, and coatings colours. The engines are mainly composed of metal (iron and copper alloys), wood, concrete, and glass. The metal and concrete parts are painted in different colours. Several international standards organizations recommend the use, in industrial environments, of a colour coding related to safety and machine function.[17–19] For example, red and yellow are used to identify hazardous areas, and orange defines dangerous parts of machines and equipment. Although these recommendations appear mainly in early 21st-century, a non-standard colour code could have existed before.
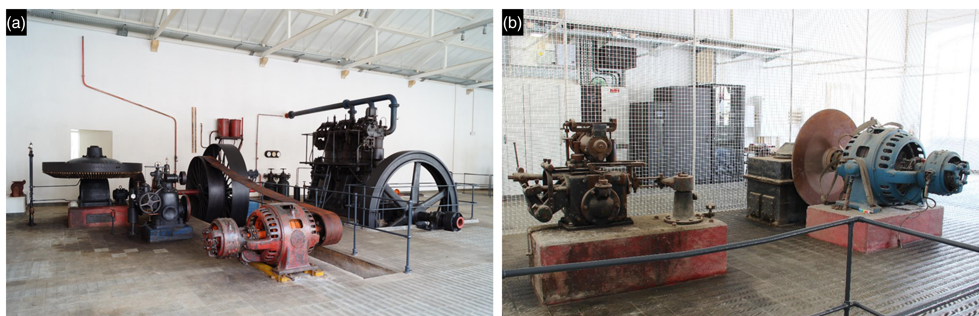
FIGURE 1 The three energy generators groups from the powerplant at Levada de Tomar, Portugal. (a) AGK hydraulic engine with a Francis-type turbine, installed in 1924, next to the 1927 SLM diesel engine. (b) O. Meyer & Co hydraulic engine implemented in 1944 (photographs M. Tissot (a) and M. Lemos (b))

TABLE 1 Identification, manufacturer, year of implementation, constitutive materials, and coating colours of the three generator groups from the powerplant at Tomar studied in this work

ID	Generator group	Manufacturer	Year of implementation	Constitutive materials	Coating colours
G1	Hydraulic engine with a Francis-type turbine	Amme, Giesecke & Konegen (AGK) (Braunschweig, Germany) Allmänna Svenska Elektriska Aktiebolaget (ASEA) (Sweden)	1924	Metal (aluminium, iron, and copper alloys); textile; wood; glass; concrete; paint; leather	Blue; red; black; yellow; orange
G2	Diesel engine	Société Suisse de construction de locomotives et de machines (SLM) (Winterthur, Switzerland)	1927	Metal (aluminium, iron, and copper alloys); wood; glass; paint	Blue; red; black
G3	Hydraulic engine with a propeller-type turbine	O. Meyer & C. (Soleure, Switzerland) ASEA (Sweden)	1944	Metal (aluminium, iron, and copper alloys); concrete; paint; leather	Blue; red; black

However, in this case, a relation between colours and engine parts was not found.

3 | EXAM AND ANALYTICAL TECHNIQUES

The study was made *ex-situ* over 29 samples collected from the three energy generators groups (Table S1). The samples were embedded in a clear casting polyester resin (MR® polyester resin). The coatings morphology and stratigraphy were observed by using a M205 C stereomicroscope from Leica and a scanning electron microscope (SEM) EVO 50 model from Zeiss, operated with accelerating voltages at 25 and 30 kV. The elemental composition of the coatings was obtained by using a μXRF and the EDS set-up of the SEM. The μXRF Tornado M4 from Bruker is equipped with a Rh target X-ray tube, coupled to a XFlash® SDD detector, with a 30 mm² sensitive area

and an energy resolution <145 eV at 5.9 keV. Outside the X-ray tube, there is a polycapillary lens that accounts for a spot size down to 25 μm at the sample. The X-ray tube operated at 50 kV and 300 μA for 120 s. The EDS spectrometer is from Oxford Instruments, model INCA x-sight coupled to the SEM, with a 10-mm² Si (Li) detector, energy resolution of 133 eV at 5.9 keV, and allowing detection of elements with Z > 4. Data were acquired with 25 and 30 kV accelerating voltages, 8.5 mm working distance, emission current adjusted to 150 μA, dead time adjusted to 12%, and 30 s live time (process time 4).

The structural composition was carried out by μRaman spectroscopy using an XploRA confocal spectrometer from Horiba-Jobin Yvon GmbH equipped with an air-cooled iDus CCD detector. Spectra were obtained using a 785 nm laser wavelength, a 100× magnification objective, a 300 μm pinhole, a 200 μm entrance slit, and a 1,200 lines/mm diffraction grating. Spectra deconvolution was performed using LabSpec (V5.78) software. The

spectrometer was calibrated with the silicon Raman band at 520.7 cm^{-1}. The pigments were identified with the Horiba Spectral ID database and by using reference spectra in the literature.

4 | RESULTS AND DISCUSSION

4.1 | Colours of the paint coatings

Table 2 summarises the identification of the pigments, used at the paint coatings, obtained by μRaman and μXRF spectroscopies.

The collected Raman spectra of blue coating samples allowed the identification of Prussian blue ($C_{18}Fe_7N_{18}$) and copper-phthalocyanine blue ($C_{32}H_{16}CuN_8$) pigments. Prussian blue is present at G1, G2, and G3 whereas blue copper-phthalocyanine appears at the 1944 generator group (G3). This can be explained by the fact that copper-phthalocyanine blue is only used, on industrial[23] and artistic areas,[24,25] since 1935, contrarily to the Prussian blue, used since middle 18th-century. Although the latter pigment has a strong reddish blue colour with good opacity, it is relatively unstable when exposed to a corrosive atmosphere.[26] The Prussian blue had a wide application in the paint industry domain, from automotive finishes[27] to industrial wallpapers.[12] However, inorganic blue pigments, like Prussian blue, were replaced by copper-phthalocyanine blues, the most common organic

pigments in the coating industry.[26] These were often chosen due to its bright blue colour, power of cover, and its stability to light and heat (up to 500°C).[23]

The results obtained suggest that the used pigments are compatible with the chronology of the equipment. Regarding G3, it is also possible to suggest that the blue parts were originally painted in Prussian blue and that were afterwards repainted with blue copper phthalocyanine, which is compatible with the period of use of the machine (1944–1990).

The red coatings of the energy generators groups are obtained by using two distinct colouring agents, red iron oxide (α-Fe_2O_3), and toluidine red ($C_{17}H_{13}N_3O_3$). The G1, G2, and G3 groups have toluidine red-based coatings, while G3 equipment has coatings composed by the two colouring agents. These are found at two parts of G3 alternator, the stator, coated using iron oxide and the lubrication lid painted using toluidine red (Figure S1). The presence of both colouring agents at G3 alternator could not be ascribed to any specific cause except being a result of maintenance action. In fact, red iron oxide and toluidine red have distinct chemical properties, applications, and chronologies. Iron oxide, an inorganic pigment, is very stable to chemicals and high temperatures (up to 1200°C in the air) and is lightfast, contrarily to the toluidine red, an organic insoluble azo dye, characterised by its low tinting strength and lightfastness.[24] Even If considered the most unstable of the two colouring agents, the toluidine red is found in the three generators groups,

TABLE 2 XRF key elements and characteristic Raman bands obtained for blue, red, yellow, orange, and black coatings, their location, assigned pigments, and references

Coating colour	Location	XRF key elements	Characteristic Raman bands (cm^{-1}) and relative intensity	Assigned pigments	References
Blue	G1; G2; G3	Fe	279(w), 539(w), 2,089(w), 2,152(s)[a]	Prussian blue	Bell et al.[20]
	G3	Cu	257(w), 486(w), 597(w), 683(s), 750(s), 956(w), 1,009(w), 1,142(m), 1,342(s), 1,454(m), 1,532(s)	Blue Cu phthalocyanine	Fremout and Saverwyns[21]
Red	G1; G2; G3	—	149(m), 286(m), 341(s), 384(m), 456(m), 617(m), 725(m), 799(m), 845(m), 988(m), 1,081(m), 1,130(m), 1,186(m) 1,217(m), 1,321(s), 1,334(s), 1,396(s), 1,447(s), 1,499(m), 1,555(s), 1,622(s)[a]	Toluidine red	Fremout and Saverwyns[21]
	G3	Fe	219(s), 238(w), 285(vs), 404(s), 491(vw) 600(m)	Red iron oxide	Bell et al.[20]
Yellow	G1	Cr, Pb	337(w), 356(s), 374(w), 401(w), 840(s)	Chrome yellow	Chua et al.[22]
Orange	G1	Cr, Pb	150(s), 337(w), 360(m), 379(w), 822(sh), 838(vs)	Chrome orange Chrome yellow	Chua et al.[22]
Black	G1; G2; G3	—	1,321(br), 1,601(br)[a]	Carbon black	Bell et al.[20]

Note: s (strong), m (medium), w (weak), v (very), sh (shoulder), br (broad).

[a]Characteristic Raman bands of the pigment spectrum selected to illustrate all those obtained for the coatings where the same pigment was identified.

suggesting a wide application in the industrial domain. In fact, in the 20th-century, organic pigments dominated the colourants market, being mostly composed by azo pigments, those that contain the azo linkage (-N=N-).[26] Toluidine red is introduced in 1905 and until the end of 1970 was one of the most used red pigments in the industrial domain.[24,25]

The alternator of G1 has yellow and orange coatings. The yellow one is composed of lead chromate ($PbCrO_4$) while the orange is a mixture of the latter and lead chromate with lead oxide ($PbCrO_4 \cdot PbO$), identified by the Raman characteristic bands at approximately 150 and 822 cm^{-1}. Lead chromate is a common yellow pigment used from the beginning of the 19th-century to provide colour and opacity to decorative and industrial undercoats and to confer bright finishes.[26] Although the references of its use as a colouring agent of historical industrial engines are inexistent, its application on industrial 19th-century wallpapers is reported.[12]

The three energy generators groups have black colour coatings. All the colours are obtained by using carbon black, an inorganic pigment insoluble in solvents, stable to acids and alkalis, and with excellent lightfastness. Carbon black is the main black pigment used in the decorative[12,25] and paint industry.[26]

4.2 | Paint systems

Coating cross-section samples were analysed to characterise the paint system used in the engines. The three generators groups show distinct paint systems, with G2 presenting the simplest. The paint components of this engine group have only one paint layer. This paint system can be ascribed either to the original paint method or to repainting actions that included removing previous coatings from the engine components. G1 presents more complex paint coatings. Figure 2A shows the coating cross section of the ASEA alternator of G1, which has five

layers. The first and the third layers are 20 μm thick and have grey colour, the second is a 160 μm yellow layer, the fourth is a 420 μm black coloured layer, and the outer layer has a red colour.

The morphology of the paint system was studied by SEM. Figure 2B of the cross-section sample shows the uniformity of the second layer and the different sizes and shapes of the pigment particles, mostly with rounded edges, of the fourth. EDS analysis evidenced the layers elemental composition, namely, the small Ti-based particles (in white) at first and third layers (Figure S2A) and the Ba, S, and Fe at the second layer (Figure S2B).

The identification of the compounds of each layer was carried out by μRaman. Figure 3A shows the Raman spectra obtained for each layer. The first and third layers show a very strong band at approximately 146 and a medium band at approximately 640 cm^{-1} distinctive of titanium dioxide (TiO_2),[28] and the carbon black characteristic broad bands at approximately 1,300 and 1,600 cm^{-1}. Data suggest that these layers are composed of a mixture of TiO_2 and carbon black, which is in accordance with their grey colour and the EDS results. The yellow colour of the second layer is obtained by mixing artificial yellow ochre ($Fe(OH)_3$), identified by the 241, 298, 393, and 547 cm^{-1} bands,[20] with barite ($BaSO_4$), with a main band at approximately 988 cm^{-1}.[20] The black colour layer is composed of carbon black identified by the 1,311 and 1,600 cm^{-1} broad bands. The colouring agent of the outer layer is toluidine red identified by comparison with a standard reference spectrum (Figure 3B).[21]

The identified pigments agree with those used in paint systems of industrial structures.[6] For instance, due to its high resistance to heat and to UV radiation, TiO_2 was traditionally used in paint coatings of industrial iron and steel substrates.[29]

It should be underlined the sequence, composition, and thicknesses of the layers. The TiO_2 and carbon black mixture layers (first and third) are thinner than the
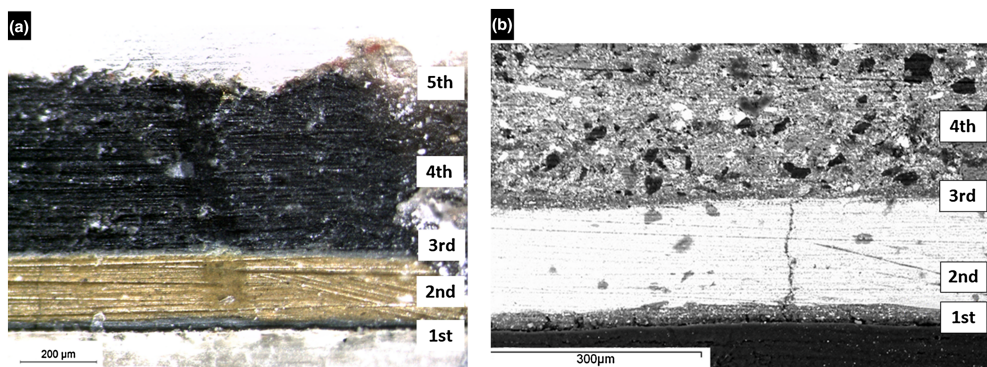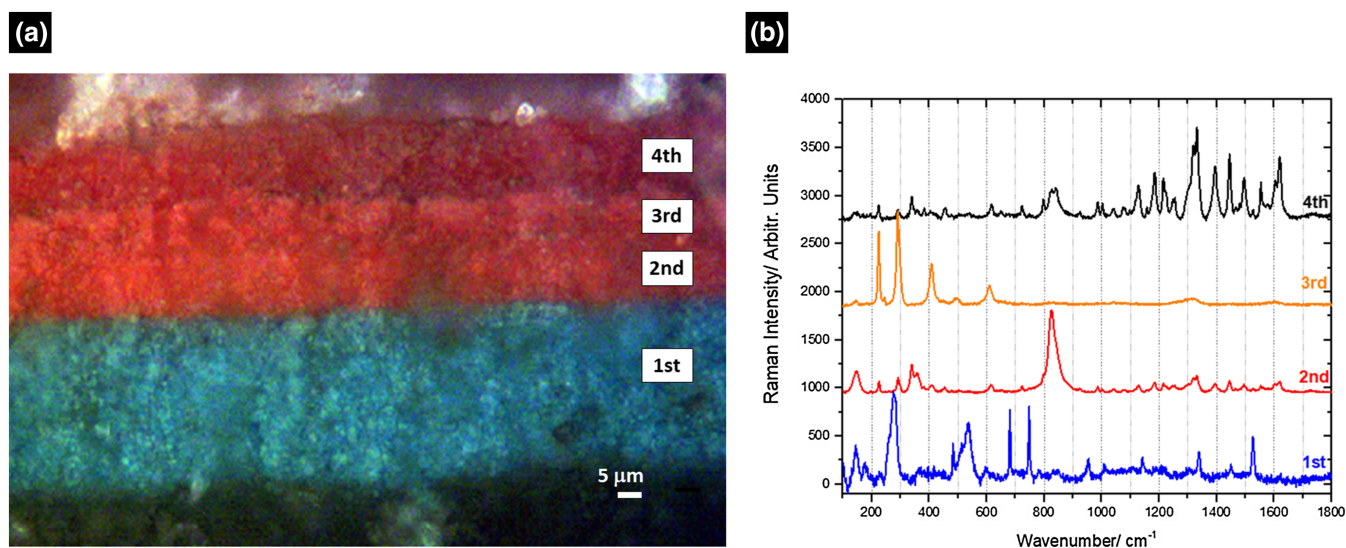

FIGURE 2 Micrography of a coating cross section from the ASEA alternator (G1) displaying the paint system composed of five layers with grey (first and third), yellow (second), black (fourth), and red (fifth) colours (a) and SEM-BSE image of the coating cross section displaying the first four layers (b)
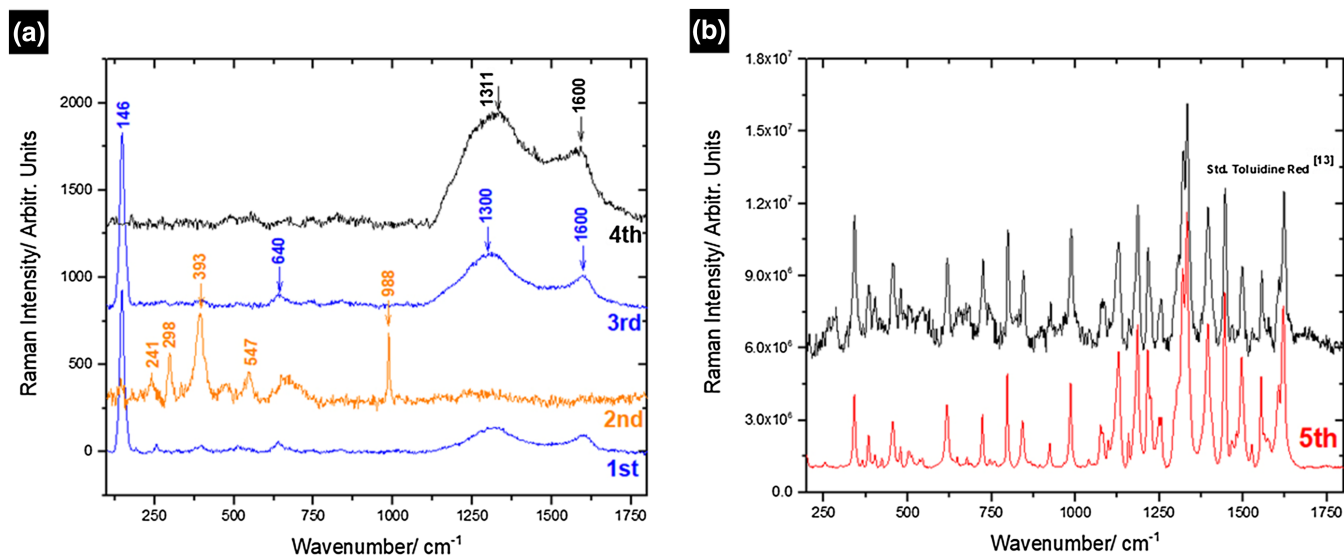
FIGURE 3 Raman spectra obtained for the first four layers that compose the ASEA alternator paint system (a) and for the fifth layer to which was added the standard reference of the toluidine red (b)[21]

yellow ochre and the carbon black ones, suggesting they were applied as preparation layers. However, it remains unclear if this multilayered system was original or if the third and fourth layers were applied together afterwards, during a maintenance action. In the latter case, the technique and the compounds used were similar. The toluidine red can be ascribed to a posterior maintenance action, as the compound is an organic azo dye, contrary to the pigments used at the other layers, suggesting the application of another painting technique.

An additional paint system was observed for the G3 alternator (Figure S1B). Figure 4 shows the cross section and Raman spectra of the red lubrication lid revealing a paint system comprising four layers. The first, with 30 μm, is composed of Cu phthalocyanine blue, followed by a 10 μm molybdate red ($PbCrO_4.PbSO_4.PbMO_4$) and by a 10 μm toluidine red layer. Between the two red layers exists a 10 μm haematite layer. It should be emphasised the identification of molybdate red, ascribed by the presence of Mo, Cr, and Pb at the μXRF

FIGURE 4 (a) Micrography of a coating cross section from the ASEA alternator (G3) revealing the existence of four layers, the first in blue and the others in red, and (b) Raman spectra obtained for each layer allowing the compounds identification as phthalocyanine blue (first), molybdate red (second), haematite (third), and toluidine red (fourth)

spectrum (Figure S3) and by the very strong band at approximately 830 cm^{-1} and by the 340 and 360 cm^{-1} bands at the Raman spectrum.[22] This inorganic pigment has a good tinting strength and good hiding power. Although being lightfast, a gradual colour loss can occur due to bleaching by sulphur dioxide due to extended exposure to industrial atmospheres.[26] Since its introduction in 1936, its application was reported in the production of paints, coatings, and plastics[27] and in 20th-century concrete on woodblock prints.[22] As the alternator cover is blue and only the lubrication lid is in red, we can suggest that first was applied a blue paint over all the surface and then a molybdate red layer was applied over the lid, becoming easier to paint. The toluidine red and the haematite layers can be a result of maintenance actions aiming the lid recoating.

4.3 | Conservation assessment of the paint coatings

The concrete and metallic parts of the three engines have paint coatings. Concerning the metal pieces, only those in iron alloys are coated, as iron is more easily corroded than copper and copper alloys, the other main metals used at the engines. The coatings applied over the iron parts show scratches and defects, and some of them developed cracks resulting in coating detachment. This phenomenon is due to the substrate corrosion, accelerated by the presence of scratches and cracks, allowing the diffusion of water and ions from the corrosive atmospheric environment to the interface between the coating and the metal substrate.[30]

The observation of detached coatings from the diesel engine revealed a black powdery layer between the coating and the metal substrate, identified by µRaman as carbon black. The presence of this compound can be due to deposits formed during the operation of the engine resulting from incomplete combustion of hydrocarbons.[31] Hoang and Pham[32] state that the formation of carbon black (black soot), and other combustion deposits, occurs at temperatures higher than 350°C. The presence of carbon black between the metal substrate and the paint coating suggests that the diesel engine operated at high temperatures during a long time and that the paint coating was not replaced after the engine shutdown.

It was also observed at some cross-section samples the existence of an interface layer between the iron substrate and paint coating composed of a mixture of corrosion products and paint coating from the yellow paint of the alternator′ base of the 1924 generator group (Figure 5).
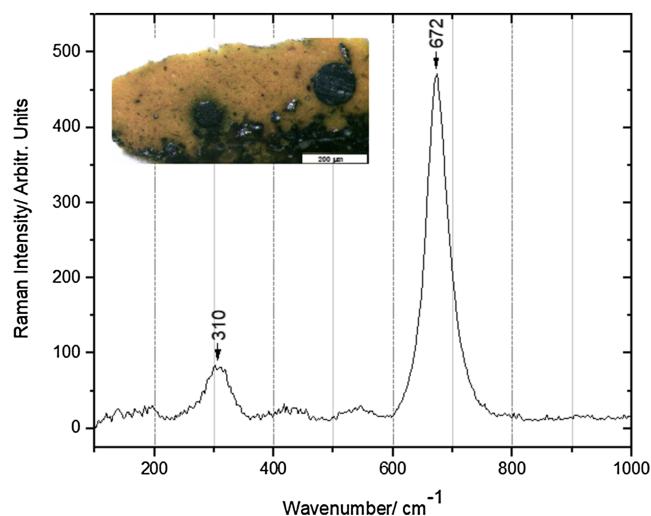
FIGURE 5 Raman spectrum of magnetite, displaying the characteristic bands at 310 and 672 cm^{-1}. Inset: Micrography of the coating cross section of the ASEA alternator base showing the chrome yellow (PbCrO$_4$) paint layer and the iron corrosion product (magnetite) in the middle of the coating

The key corrosion product identified by Raman is magnetite (Fe$_3$O$_4$) characterised by the spectrum band[33] at 672 cm^{-1} (Figure 5). Iron corrosion products resulting from atmospheric corrosion are mainly composed by a mixture of oxides and hydroxides. These compounds can be converted, by heating or electrochemical reactions, from one phase to another being sometimes difficult to distinguish between them.[33] For example, maghemite (γ-Fe$_2$O$_3$) can be formed by heating magnetite at 60°C. Maghemite shows Raman spectra bands at 385, 505, 670, 710, and 1,360 cm^{-1} whereas magnetite has only one main band at 670 cm^{-1}.[34] That means if a Raman spectrum shows more bands than the 670 cm^{-1} one, the corrosion is composed by maghemite or by a mixture of maghemite and magnetite. Considering that only magnetite has been identified as corrosion product, we may suggest that corrosion developed after the engine shutdown and not while the engine was in operation, when the surface could reach temperatures above 60°C.

5 | CONCLUSIONS

The energy generators of the powerplant at Levada de Tomar, Portugal, are representative of the historical industry of electricity production. The characterisation of their paint coatings allowed increasing knowledge on the colouring agents used in industrial context in the early 20th-century. Although, the identified pigments are in accordance with those used in the industrial context, referenced in specialised books, reports of their use as a colouring agent of industrial heritage engines are scarce.

The paint system study has shown the use of complex paint techniques, allowing to infer on equipment maintenance actions and on the conservation assessment. Complex paint systems with more than one layer, including preparation layers, are observed for the oldest equipment (1924). For a complete characterisation of the paint systems, it is needed the identification of binders and the comparison of the results with other studies. However, the latter are scant, hampering a sustained interpretation of the paint systems.

Equipment maintenance actions, that is, recoatings, were observed for the equipment working for a longer period (1944–1990), including pigments with different chemical properties, applications, and chronologies. Powdery carbon black layers resulting from incomplete hydrocarbon combustion were identified between metallic substrates and coating layers. This indicates that after the powerplant shutdown, the paint coatings were not replaced. The presence of magnetite, as a corrosion product of iron alloy substrate, indicated that corrosion developed after the engine shutdown and not while the engine was in operation.

With this work, we demonstrated the relevance of the scientific-based study of paint coatings. The multianalytical approach allowed the identification of the pigments, providing a chronological chromatic pallet, and to increase knowledge on the use and maintenance of the engine. The obtained results can also be used for the implementation of conservation programmes, as the detailed knowledge of coatings composition allows to define the accurate materials to be used in current and future actions.

We also demonstrated the potential application of a µRaman spectrometry to Industrial Heritage study. Furthermore, we draw attention to the need for comparative studies and to the creation of databases for sustained coating information applied to IH that will contribute to its knowledge and preservation.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.