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Historical primers and paints used for aeronautical protection and colouring during WWII: a multi-techniques approach on archaeological parts.

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Abstract: Aeronautics for military or civil applications effectively pushed scientists, engineers and industrial leaders to invent and produce increasingly efficient materials. Aluminium alloys are among the most important strategic materials used in aircraft manufacturing. Consequently, so are the protective coatings (primers and paints). After decades of burial, World War II (WWII) wrecks provide a tremendous amount of archaeological information on this period of intense technological research. In this article, the original protective coatings of ten samples collected on WWII wrecks and one collection aircraft were studied. Information was retrieved thanks to a multi-techniques approach: SEM-EDS, Raman spectroscopy and XRD to identify the nature of the mineral compounds (fillers and pigments) and FTIR, Py-GC-MS and NMR to identify the organic binders of the paints and primers. This information will help conserve this valuable 20th century Industrial Heritage.

Keywords: primer, paint, aluminium alloys, historical aircraft, nitrocellulose paint

1. Introduction

Historical aircraft are part of the 20th century's Industrial Heritage. Often conserved in Air museums or by associations worldwide, they are a valuable testament to the adventure of human flight and the development of the aeronautical industries. Their constituent materials, as well as the associated technological know-hows, should thus be documented and preserved to the greatest extent possible. This work can be done by retrieving information from constructors' archives, which are often scattered or lost, as well as studying collected materials from the aircraft themselves [1, 2]. In the European project JPI-CH "PROCRAFT"¹, a corpus of 34 World War II (WWII) aircraft, primarily fighters and bombers, was assembled

¹ Protection and Conservation of Heritage Aircraft, 2020-2023, funded by JPI-CH

including numerous wrecks excavated from various fields (terrestrial, sea or lakes) in France and Italy. This is a fantastic opportunity to identify and recover as much information as possible about the original materials of historical aircraft [3].

The hulls and frames of military aircraft from this time period are mostly made of aluminium alloys from the Duralumin family (equivalent to the 2xxx family nowadays). Duralumins are sensitive to corrosion despite being very resistant mechanically, and this was an early concern of aircraft manufacturers as soon as the all-metal airplanes were produced in the early twentieth century. Several coating techniques were tested for aircraft protection against corrosion including primers and paints of various types, chemical/anodic oxidation, cladding with pure Al [4] or electrodeposited metals. Detailed information can be found in [5] and [6]. The protective coatings had to exhibit qualities of adhesion, flexibility (when subjected to vibrations or sudden temperature changes), resistance to heat, humidity or even chemicals and of course ageing resistance. An appropriate surface treatment was applied depending on the role or location of the part in question as well as the type of environment with which it was confronted during aircraft operation (marine, tropical, terrestrial, *etc.*). WWII aircraft provide a perfect illustration of this panel of protective coating [3]: Al cladding was widely applied on rolled products (plates and sheets) and anodic oxides for forged or extruded products (as well as rolled products). Various organic-based primers that were directly applied to the naked metal were also discovered. In this case, the primer served two functions: it ensured paint adhesion and it protected against corrosion. Of course, the choice of protection was also influenced by the countries' technological advancements. This is especially true for the binder, which is the main component of a paint or a primer. Natural products were initially used as the binder. Tar pitch or asphalts, for example, were tried in the beginning, as were vegetable oils and natural resins mixed with other components [7] [8, 9]. However, as the chemical industry developed, synthetic products were quickly introduced in paints. Semi-synthetic resins first appeared (for example, nitro or acetyl-cellulose or oil-derived products), followed by synthetic resins: phenoplast resins (phenol-formaldehydes), alkyds (glycerol-phthalic resins, Glyptals) [10] and later polyvinyl, polyacrylic or polyurethane resins. Many mineral compounds were used as fillers and pigments. In the particular case of corrosion inhibitor pigments [11], chromate-based compounds were used. They included zinc chromate [12], zinc-potassium tetroxochromate [13], potassium chromate $K_2Cr_2O_7$, barium chromate, strontium chromate, lead chromate [14] and others...

After decades of usage, abandonment and/or repainting campaigns by volunteers' associations in the case of collection aircraft, the original protection deposited on the alloys is frequently lost and at best, difficult to identify. Although little of the original surface of the aircraft wrecks remains due to their long stay on the ground or in the sea, these remains are a rare and highly valuable cultural testimony of the technological solutions used by manufacturers. It is even more significant because industrial secrets were common during WWII and shortage of raw materials forced industrials to change the composition of their paints [15].

2. Research aim

This article focuses on the identification of the primers and paints used by various nations involved in WWII, with the goal of highlighting each country's advancements in terms of corrosion protection of aluminium alloys in aircraft construction. It will eventually aid conservation decisions for example, applying appropriate protection (durable, reversible, compatible and not changing the aesthetical properties) to these artefacts. Understanding the original nature of the painting system will guide the choice of the type of protection that will be employed.

The mineral compounds (pigments and fillers) and the organic binder of painting systems were analysed in this article for two French, four German, two American and one Italian aircraft wrecks (airwrecks) from WWII, as well as one French collection aircraft from 1951. Several analytical and structural techniques were used to identify mineral compounds: Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) for the nature and location of elements within the paint layers, micro-Raman spectroscopy, and X-Ray Diffraction (XRD) for the structural information and thus identification of mineral compounds. As for the organic binders, Fourier-Transformed Infrared Spectroscopy (FTIR) was carried out on all samples. It is important to note that some pigments and fillers can respond in FTIR, complicating organic compound identification. When it was possible, the pigments were identified. Because of chemical evolution of the compounds, sample degradation over time can also make FTIR spectra difficult to interpret. FTIR was therefore completed for one sample by Pyrolysis coupled with Gas Chromatography Mass Spectrometry (Py-GC-MS) and Nuclear Magnetic Resonance (NMR). These three techniques are complementary for organic binder identification as explained in section 4.2.

This multi-technique approach was used to identify the main components of the paints of ten WWII airwrecks as detailed below. By comparing and correlating them with archives, it is demonstrated that countries can share common procedures in terms of mineral compounds or organic binders' selection, reflecting the historical context in which protective coatings were produced and applied.

3. Experimental/sampling strategy and methods

3.1. Presentation of samples

The corpus is presented in Table 1. It includes ten samples from various aircraft wrecks kept and maintained by associations across Europe. The French wrecks (Dewoitine D.520, Latécoère 298) and the German wrecks (Dornier 217, Heinkel 111, Heinkel 177 and Junkers 88) were all excavated by the association Aérocherche in terrestrial sites (mainly sites in the French Pyrenees mountains). The Morane Saulnier 733 was recovered at the end of its lifespan and is now maintained by Les Ailes Anciennes Toulouse (France). The American Lockheed P38 Lightning wreck was found near Laval in Normandy (France) and maintained by DRAC Pays de Loire. The Republic Aviation P-47 Thunderbolt was excavated from the sea in Italy (Cagliari) by the association Air Club & Fun and the Macchi MC202 wreck was recovered by Volandia in Italy (near Baglioni).

The artefacts were selected because they are all made of wrought aluminium alloys and have residues of original paint. After being excavated, the artefacts received no treatment except for a simple tap-water wash and brushing to get rid of the concretions.

The MS733 is the only collection aircraft that is not a wreck: it was repainted at several occasions. For comparison purposes, a protected area on the inside of the central wing section was selected. On this fragment, the original paint is conserved over a large area.

Table 1. Aircraft wrecks considered for the study, classified under the country of aircraft production. Information on the excavation sites and the type of available artefacts are provided.

Country	Sample number	Aircraft (Year of production)	Excavation site / landfill type	Type of available artefacts
Germany	DO217	Dornier 217 (1943)	Sacoué, France / terrestrial	Fuselage (fragments)
	JU88	Junkers 88 (1943)	Pechbusque, France/ terrestrial	Engine cowl (fragment)
	HE177	Heinkel 177 (1943)	Uchaq-Parentis, France/ terrestrial	Fuselage (fragment)
	HE111	Heinkel 111 (1937)	Tarbes, France/ terrestrial	Stringer
France	LA298	Latécoère 298 (1940)	Fougax, France/ terrestrial	Fuselage (fragments)
	DE520	Dewoitine D520 (1940)	Encausse-les-Termes, France/ terrestrial	Fuselage (fragments)
	MS733	Morane et Saulnier 733 (1951)	Toulouse, France/terrestrial	Central wing section
USA	LOP38	Lockheed P38 Lightning (1944)	Laval, France / sea coast	Propeller blades
	RAP47D	Republic Aviation P-47D Thunderbolt (1943)	Bagnarola di Budrio, Italy / terrestrial	Fuselage (fragments), Stringer (fragments)
Italy	MAMC202	Macchi MC 202 (1942)	Cagliari, Italy / sea	Wing spar, wing ribs

Samples around 0.5 cm² to 4 cm² area were mechanically collected from aircraft fragments with a rotary tool or a saw in the area of least damaged paint. For XRD analysis, samples were analysed with no further preparation except removing of dust. For FTIR, NMR and pyrolysis GC-MS, paint was taken from its substrate with a scalpel after cleaning with a brush and wet cotton for dirty samples. Layers were separated from each other and from the primer when it was possible. Observations with optical microscope and SEM-EDS were made on cross section samples embedded with cold curing epoxy resin. They were polished mechanically with SiC paper from grades 600 to 1200. Then, an extra polishing of the aluminium substrate was made with diamond abrasive pastes of 3 µm and 1 µm particle size to obtain a mirror-like finish.

3.2. Methods

Optical microscopy

Stratigraphy of samples was determined with Eclipse MA200 microscope (Nikon, Japan) on embedded samples. All pictures were taken with the following parameters: in dark field with the same level of brightness.

SEM-EDS

The elemental analysis was conducted through scanning electron microscope (SEM) on a Helios Nanolab 600i (FEI, USA) with an accelerating voltage applied between 15 keV and 20

keV, an electron beam intensity between 0.34 and 0.69 nA and an energy dispersive X-ray spectrometer (EDS) X-MAXN 150 microprobe (Oxford Instruments, U.K). Cross-sections were carbon coated to make them conductive. In addition, SEM observation and elemental analysis were also performed on a SEM ZEISS Evo25 Variable Pressure apparatus coupled with a Quantax 200 EDS system (Bruker) using a XFlash 6/30 SDD detector.

XRD

The mineral identification compounds were performed using a D8 Discover (Bruker AXS, USA) diffractometer equipped with a Co micro-source and a 2D detector.

The sample was positioned on an x,y,z table allowing us to select the analysed area using a laser and an optical camera. The pattern is obtained by assembling a series of images recorded at different positions. A 1 mm diameter collimator was used and the images were recorded from 20° to 80° every 15°. 1D XRD pattern is obtained after the integration of selected zone.

Raman

The embedded cross sections were analysed with an XploRA (HORIBA, Japan) spectrometer coupled with a confocal microscope for precise positioning (spatial resolution about 2 µm) and equipped with a Peltier cooled CCD detector. A green laser (532 nm) was used with a 1800 diffraction grating giving a spectral resolution of 2 cm⁻¹. The acquisition time per scan was between 20 and 60 seconds depending on the fluorescence of the target coating and 2 to 4 scans were acquired per spectrum.

FTIR

Removed flakes of paint were analysed in FTIR spectroscopy by transmission on a Nicolet IS50 (ThermoFisher, USA) spectrometer. Approximately 1 mg of paint was mixed with 300 mg of dry KBr into a pellet of 18 mm diameter and 1 mm thickness. 64 scans were acquired for each spectrum. The spectra range used was 4000-400 cm⁻¹ with 4 cm⁻¹ resolution.

NMR

An NMR analysis was performed only on the beige paint of the sample MS733. NMR spectrum was acquired on BRUKER spectrometer operating with Advance NEO console at 300 MHz for all spectra at 298 K. 1D-NMR and 2D-NMR experiments were: ¹H, ¹³C, heteronuclear single quantum correlation spectroscopy (HSQC) and heteronuclear multiple-bond correlation spectroscopy (HMBC) from ¹H–¹³C. The chemical shifts (δ) have been reported in ppm calibrated with the solvent resonance as the internal standard CDCl₃ and DMSO-d₆. The solutions were filtered on Célite® to remove eventual aluminium residue that can intercept binder signals.

Pyrolysis-GC/MS

A pyrolysis GC-MS was performed only on the sample MS733. The experiment was performed on a CDS Probe 6150 pyrolysis (CDS Analytical, USA) and a Clarus 580 chromatograph (Perkin Elmer, USA) connected to a Clarus 560 S mass spectrometer (Perkin Elmer, USA). A 5% Ph Me Silicone cross-linked Elite HP-5MS capillary column (40 m x 0.18 mm x 0.18 µm) and helium as vector gas were used. The sample was heated at 550°C in the pyrolysis. The washing with

dichloromethane was done after removing the paint from the substrate. Extraction, agitation, US filtration were repeated several times until no dry residue remained in the extracted part

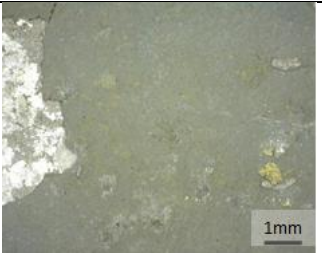
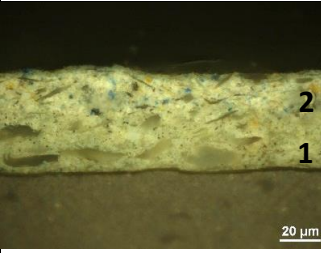
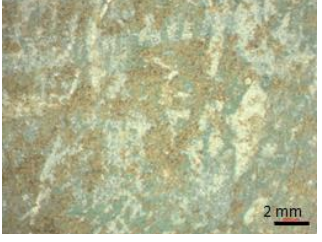
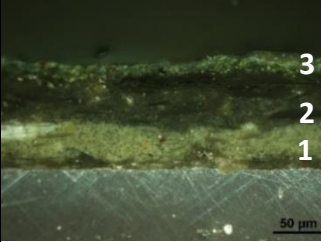
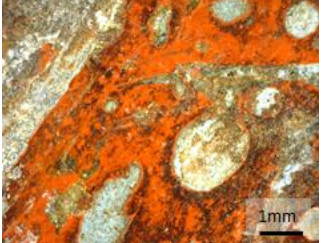
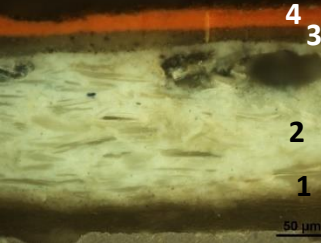
4. Results

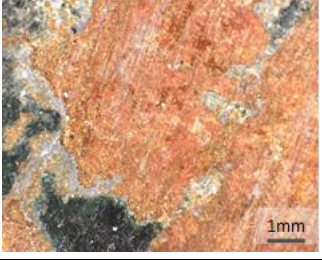
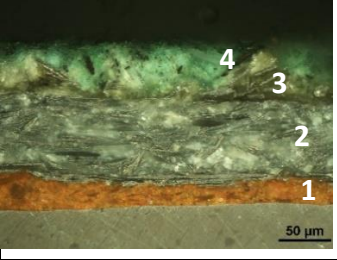
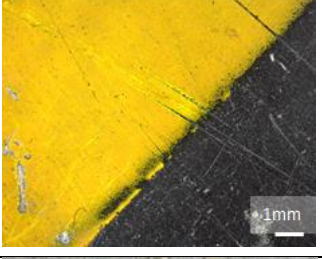
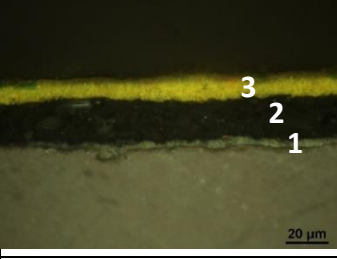
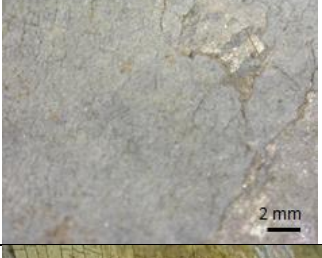
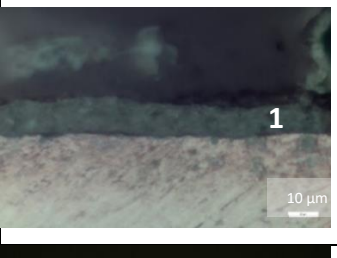

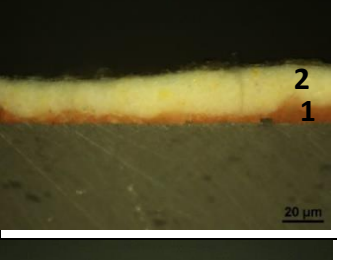
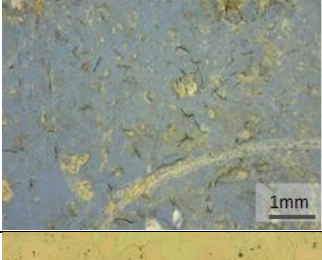
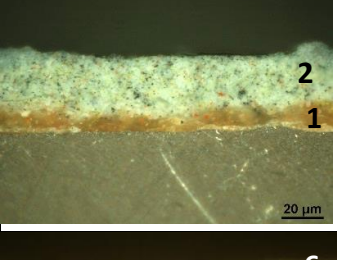
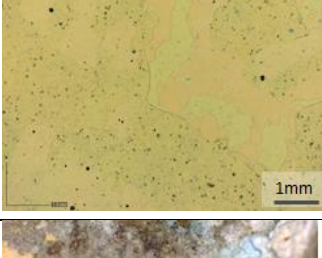
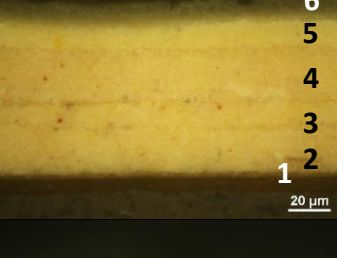

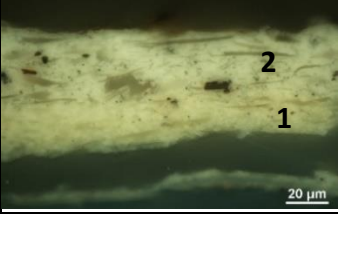
A paint is composed of organic compounds (including binders, additives, solvents) on the one hand and mineral compounds in the other hand. Among mineral compounds, one can distinguish pigments (for colouring and for corrosion inhibition purposes) and fillers (for opacity/barrier effect and to obtain the desired texture). Fillers and pigments were analysed and identified first (section 4.1) followed by the identification of the organic binders (section 4.2).

4.1. Identification of mineral compounds: fillers and pigments

Table 2 depicts the surface and cross-section of the samples as seen through optical microscopy. Information is also provided on the nature of the mineral compounds contained in the primer and paint layers. The supplementary information A contains detailed and additional results for the investigated aircraft. Paint layers will be discussed first because they are easily observable by optical microscopy, followed by primers, which are the first layer in contact with the metal and sometimes more difficult to detect.

Table 2. Optical microscopy images of the surface and the cross-section of the studied samples. Information on the thickness and the composition of each layer is provided in the last column.

Sample	Surface	Stratigraphy : colour / thickness / minerals	
Germany			<p>2. Green / 22 µm / Talc, anatase, barite</p> <p>1. Light green / 28 µm / Talc, anatase, antimony oxide</p>
			<p>3. Green-silver / 13 µm / Anatase, quartz, barite</p> <p>2. Dark grey / 48 µm / Talc, lead chromate</p> <p>1. White / 42 µm / Talc, zinc chromate, zincite</p>
			<p>4. Red-orange / 17 µm / Hematite</p> <p>3. Transparent / 19 µm / No charge</p> <p>2. White / 147 µm / Talc, zincite, barite</p> <p>1. Primer / 25 µm / Zinc-potassium tetroxychromate</p>

		HE111			<p>4. Dark green / 13-50 μm / Talc, lead chromate</p> <p>3. Light green / 5-50 μm / Talc, lead chromate</p> <p>2. Silver / 60-80 μm / Talc, zincite, Al platelets</p> <p>1. Red (primer)/ 25-40 μm / Talc, lead chromate, hematite</p>
USA		LOP38			<p>3. Yellow/ 12 μm / lead chromate</p> <p>2. Black / 18 μm / Carbon black, magnesium-silicates, quartz</p> <p>1. Grey-green (primer)/ 4 μm / Zinc chromate</p>
		RAP47D			<p>1. Blue / 25 μm / Anatase, quartz, cristobalite</p>
France		DE520			<p>2. Beige / 20 μm / Anatase, zincite, lead chromate, quartz</p> <p>1. Red (primer) / 4-10 μm / Zinc-potassium tetroxochromate, hematite</p>
		LA298			<p>2. Blue / 26 μm / Anatase, lead chromate, quartz</p> <p>1. Red (primer) / 9 μm / Zinc-potassium tetroxochromate, hematite</p>
		MS733			<p>6. Transparent-beige / 10 μm</p> <p>5. Beige / 12 μm / Rutile, lead chromate, hematite</p> <p>4. Beige / 26 μm Rutile, zincite,</p> <p>3. Beige / 12 μm lithopone, hematite,</p> <p>2. Beige / 22 μm lead chromate</p> <p>1.Green / <1 μm Zinc chromate + P</p>
Italy		MAMC202			<p>2. White / 34μm / Anatase, talc, quartz</p> <p>1. Beige / 22μm / Anatase, talc, quartz</p>

The optical observations revealed differences in the stratigraphy of the studied paint based on the location of the fragment on the aircraft:

- On fragments that were collected on the main body/fuselage (case of the DE520, LA298, RAP47D or MAMC202) or in the interior of the aircraft (case of the DO217), there are only two layers (including the primer).
- More than two layers are commonly found on the exterior of the aircraft where camouflage was applied (as in the case of the JU88 or the HE111) or in specific areas such as markings (as in the case of the HE177 and the LOP38).
- In the sole case of the MS733, up to 6 layers are present. We think that only layers 1 (primer), 2 and 3 are the original ones whereas the upper layers (4, 5, 6), which are not very adherent, were applied later. These repainting layers are frequently encountered in collection aircraft.

On the painted German aircraft fragments (DO217, JU88 and HE111), the most widespread colour is the military green corresponding to usual camouflage colour applied by the German forces during WWII. For fillers, talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) is found in the four German aircraft fragments, whether in the primer or in the paint layers. The talc grains are acicular with sizes going up to several tens of microns (see Figure A.1. in supplementary information). Other fillers are identified such as aluminium platelets in the case of the (HE111). The latter was widely used in the aircraft industry worldwide since the 1910s (Zeppelin airships).

Anatase (TiO_2), present as submicron particles, was used to colour the layers. This white pigment was synthesized for the first time in 1916. Anatase was combined with barium sulphate (barite) [16], as appears to be the case for all post-1940 German aircraft (DO217, JU88 and HE177). Lead chromate (PbCrO_4) (yellow) is present in the green layers, most likely mixed with an unidentified blue pigment. Antimony oxide (Sb_2O_3 , either as senarmontite or valentinite) is found in the DO217 primer: it is known to be a white pigment in paints usually mixed with anatase or zincite [17]. Eventually, hematite is the pigment that gives the HE177 top coating its red colour.

Regarding primers, the first light green layer of the DO217 contains talc, anatase and antimony oxide. However, in this sample no inhibitive pigment was found. On the next two German aircraft samples (JU88 and HE177), the primer is a very thin layer, hard to detect with optical microscopy. As an inhibitive pigment, the light green layer for the HE177 contains a zinc-potassium tetroxochromate ($4\text{ZnCrO}_4 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$ [12]) and the white first layer of the JU88 contains a zinc chromate (ZnCrO_4). The only clear and distinct primer is on the HE111 sample which comes from a Heinkel 111 fighter from 1937. The primer is indeed relatively thick (25-40 μm) and red. The red colour is due to the hematite pigment. The inhibitive pigment found in the HE111 sample is a lead chromate (PbCrO_4).

For American aircraft, the two studied samples were collected on parts with different mechanical purposes. The painted sample LOP38 comes from a propeller blade. The yellow paint was commonly applied to the ends of the blades (which were all painted in black) for safety reasons during usage. Lead chromate is the mineral compound that provides the yellow colour (as for the German aircraft). Carbon black was identified as the pigment in the black

paint. The fillers in this black layer are quite large crystals (several tens of microns sometimes) as shown in Figure A.5 in supplementary A. They belong to the magnesium-silicate class and amphiboles group. They are either tremolite ($\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$), richterite ($\text{Na}(\text{Ca},\text{Na})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$) or edenite ($\text{NaCa}_2\text{Mg}_5\text{Si}_7\text{O}_{22}(\text{OH})_2$) as fingerprints in XRD and in Raman spectroscopy are similar. Another type of magnesium-silicate is identified: anthophyllite ($\text{Mg}, \text{Fe}^{+2})_7 \text{Si}_8\text{O}_{22}(\text{OH})_2$). Quartz is also present: it is generally present in the sedimentary rocks containing tremolite.

The blue paint on the RAP47D aircraft is quite thin and damaged. It is composed of anatase and different forms of SiO_2 (quartz and cristobalite) for the filler. The blue pigment was not identified yet.

In the primer of the LOP38 sample, the inhibitive pigment is a zinc chromate which was widely used in the US aircraft industry since the early 1930s [8, 18]. No inhibitive pigment was found on the RAP47D sample collected on the American aircraft.

Regarding the French aircraft fragments, the beige paint (also called *chamois* colour) on the DE520 is typical of Dewoitine paintings [19]: it contains lead chromate as a yellow pigment and anatase and zincite (ZnO) as white pigments. The blue paint on the LA298 is also typical of the seaplanes produced by Latécoère. The blue pigment has yet to be identified. This layer contains also lead chromate (yellow pigment). The white pigment, anatase, is the same as in the DE520. On both aircraft, the primer, already studied in [20], contains hematite (for the red colour) and zinc, potassium tetroxochromate ($4\text{ZnCrO}_4 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$) as an inhibitive pigment. It is similar to the primer found in the HE111 sample (from the German Heinkel 111 aircraft).

The MS733, while having a similar chamois colour as the DE520, has a slightly different composition: aside from lead chromate, which is common to both aircraft, TiO_2 rutile instead of anatase, zincite (ZnO) and lithophone (BaSO_4 , ZnS) were used either as filler or white pigments and a few grains of hematite were added to the paint. Lithopone is a white pigment that replaced white lead in the early 20th century [21]. Eventually, the primer layer on the MS733 is very thin (not visible in the optical microscope image) and contains zinc chromate as an inhibitive pigment. Phosphorous is also present, associated with oxygen and chromium (see Figure A.9.f in supplementary information A) on the surface of the aluminium. This phospho-chromo-resin compound may be the result of a phosphate primer, which may correspond to a “wash” primer (introduced during WWII by Americans and already found in French aircraft Breguet from 1958 [6]).

On the Italian aircraft (MAMC202), the paint is really damaged and mixed with corrosion products (Nordstrandite was detected by XRD, as shown in Figure A.10.e). Nevertheless, it was possible to identify talc as the filler and anatase as the white pigment. However, no primer could be clearly identified.

4.2. Identification of organic compounds: binders and plasticizers.

In paint composition, although the binder is the major compound, it is rarely unique. In fact, a mixture of binders is frequently used, and additives such as plasticizers are usually added. These are the principal organic components that can be present and detected after drying.

Solvents are added for paint application but they evaporate during drying and are usually undetectable.

In a first approach, the acquired FTIR spectra were compared with literature references of binders alone, *i.e.* nitrocellulose and alkyd resin in particular. And because identifying the functional groups is not sufficient to conclude on the nature of the organic components, FTIR was completed by two other analytical techniques (Py-GC-MS and NMR) for one sample (MS733). Py-GC-MS is a technique where the molecules are cleaved. It is then the fragments coming from the resin and/or the additives which are detected. In NMR, on the other hand, the whole molecules are conserved. The analyst is placed in a liquid to help motion of the molecules. Even complex structures can be analysed. Precise and unique displacement are then attributed to atoms present in the molecules which helps to confirm the presence of those molecules.

The painted area on the MS733 sample is sufficiently large to take enough material for carrying out the three techniques mentioned. This sample will be used as a reference for the rest of the corpus. The samples in the rest of the corpus are indeed too small, so only FTIR analysis was performed and spectra were interpreted by comparing them to the MS733 spectrum.

4.2.1. The case of MS733 sample.

FTIR

The beige layers of MS733 paint were analysed separately by FTIR. The corresponding spectra are identical for all layers. Thus, in Figure 1, only spectrum of layer 2 is shown in details. Table 2 summarizes the main identified peaks and corresponding assignments following literature's reports.

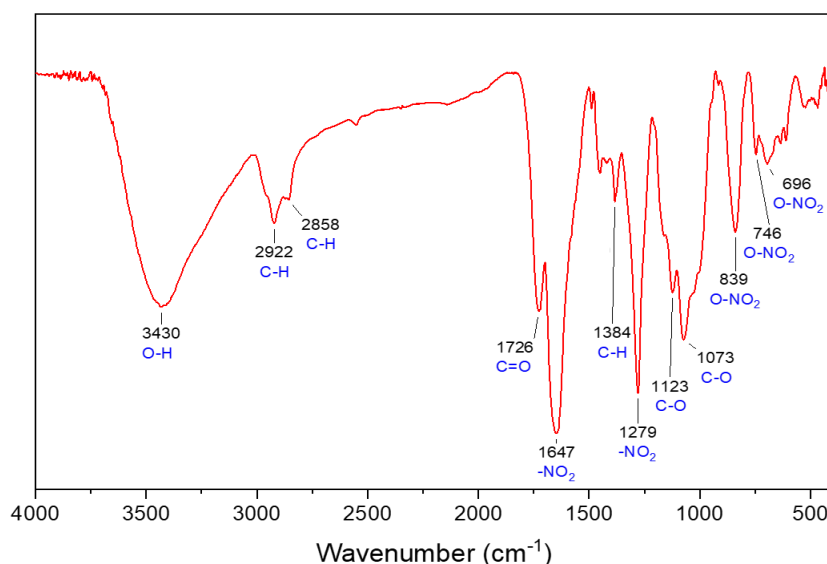


Figure 1: FTIR spectrum (arbitrary units on the Y-axis) of MS733 paint

On the FTIR spectrum of the MS733 paint, the broad band at 3430 cm⁻¹ is related to a hydroxyl stretching vibration. The vibration bands at 2925 and 2850 cm⁻¹ are related to C-H stretching in CH and CH₂. Absorption bands at 1647, 1279, 839, 746 and 696 cm⁻¹ were clearly assigned to the nitro group (NO₂) as described in Table 2. With those elements, we concluded that the main binder of this sample must be nitrocellulose. The band at 3430 cm⁻¹ could be associated

to -OH group from either decomposition of nitrocellulose (release of NO₂ group) or from the uncompleted nitration of cellulose during the production process.

Other bands remain, attributed to other organic compounds. The band at 1073 cm⁻¹ could be attributed to C-O bonding into phthalate group [22] or an unsaturated aromatic in plane deformation in phthalate or alkyd resin [23]. The band at 1123 cm⁻¹ could be attributed to C-O bonding possibly in a pyranose cycle [24] but also present in alkyd resin or phthalates [22, 23]. The signal at 1726 cm⁻¹ is characteristic of C=O bonding into ester function. This could be ascribed either to phthalate type plasticizer or alkyd resin [25, 26]. Some other references attribute this band at 1726 cm⁻¹ to the decomposition of nitro groups [27, 28]. With the identification of these additional bands, we can only conclude that alkyd resin and/or phthalate type plasticisers are present as additional compounds of the paint. Indeed, nitrocellulose was very often mixed with plasticisers (of many various types) to improve its viscosity and overcome its brittle nature [29, 30].

As characteristic functions of alkyd resin are also present in phthalates, FTIR technique alone cannot differentiate between an alkyd resin and phthalates plasticisers. The techniques of Py-GC-MS and NMR were hereafter used to clarify this point.

Table 3. FTIR bands detected in the MS733 sample and identified thanks to previously published work.

Absorbance frequency (cm ⁻¹)	Assignment	Compound associated	References
3430	O-H stretching	Nitrocellulose	[24] [28] [26]
2922-2858	C-H asymmetric and symmetric stretching in -CH and CH ₂	Nitrocellulose/ alkyd resin/ phthalate	[28] [24] [23]
1726	C=O stretching	Nitrocellulose	[27] [24]
		Alkyd resin and/or phthalate	[25], [26]
1647	-NO ₂ asymmetric stretching	Nitrocellulose	[27] [25] [24] [28] [31] [26]
1384	-CH bending	Nitrocellulose / alkyd resin / phthalate	[25] [16] [28] [26]
1279	-NO ₂ symmetric bending /stretching	Nitrocellulose	[27] [25] [24] [28] [31] [26]
1123	C-O-C symmetric stretching	Nitrocellulose (pyranose cycle)	[24] [28]
		Alkyd resin and/or phthalate	[23] [22]
1073	C-O stretching	Nitrocellulose or phthalate	[25] [28] [26]
	C=C unsaturated in-plane deformation	Phthalate	[22]
839	O-NO ₂ stretching	Nitrocellulose	[25] [28] [31] [26]
	N-O stretching	Nitrocellulose	[24] [27]
746	O-NO ₂ asymmetric deformation	Nitrocellulose	[25] [24] [28]
	Aromatic out of plane bending	Phthalate	[22]
696	O-NO ₂ symmetric deformation	Nitrocellulose	[25] [24] [28]

Pyrolysis-GC/MS

Figure 2 depicts the pyrograms of the MS733 paint for the as-received sample (a) and after dichloromethane washing (b). Identification was possible thanks to database search. The peaks at 2.30 and 2.60 minutes could be attributed to nitrocellulose, despite the fact that this compound does not respond well to pyrolysis-GC/MS due to thermal decomposition [29]. On the other hand, DEEP (Di(2-ethoxyethyl) phthalate) and DEHP (Di(2-ethylhexyl) phthalate) phthalate type plasticisers were clearly identified at respectively 25.05 min and 28.64 min. Plasticisers were dissolved after washing the paint with dichloromethane, as shown in Figure 2.b. Phthalates fragments (phthalic anhydride at 16.27 min) remain. The origin of these phthalates' fragments could be an alkyd resin. However, to confirm this hypothesis, a derivatization technique (methylation for instance) should be applied to better detect fatty acids present in oil-modified alkyd resins (typically stearic and palmitic acids) [23].

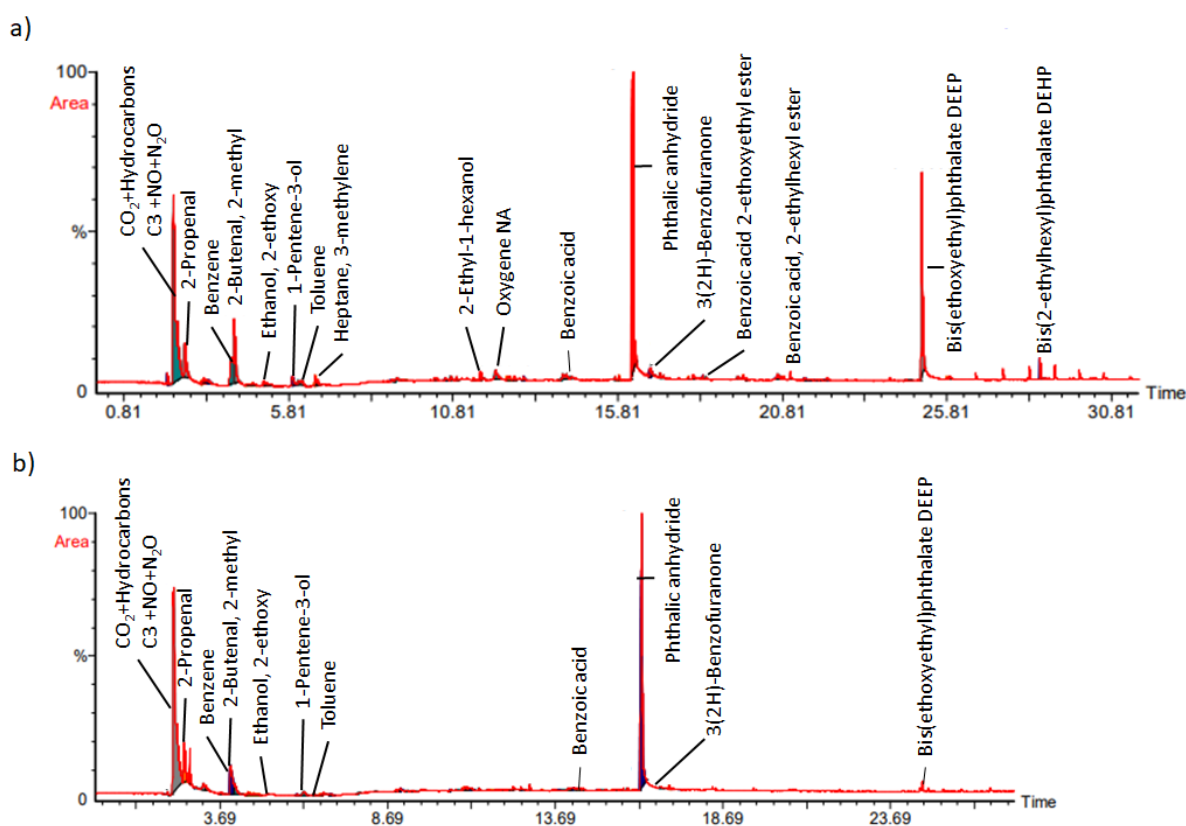


Figure 2. Py-GC-MS Pyrograms a) as-received MS733 sample, b) after extraction (dichloromethane washing)

NMR

The spectra can be found in supplementary information B. Simple and rapid acquisition of ¹H spectra (Figure B.1) exhibits low intensity signals making detection of interesting signals imprecise. Increasing the number of scans and switching to different NMR sequences help to obtain more information (Figure B.2 to B.4).

Certain information is obtained from heteronuclear single quantum correlation spectroscopy (HSQC) and heteronuclear multiple-bond correlation spectroscopy (HMBC) resulting in 2D NMR spectra with δ ¹³C-¹H (ppm) pairs. Higher displacement signals (carbonyl function with quaternary carbon or carbon included in an aromatic ring) can be attributed to either DEHP or alkyd resin. On the HSQC spectrum, DEHP is identified for 168-4.35, 133-7.8, and 68-4.35 as

well as in the HMBC spectrum at 129-7.4; 132-7.3; 11-0.85; 15-0.8; 17-1.4; 21-1.5; 23-1.7 and 25-1.8 ppm. Couples with a $\delta^{13}\text{C}$ value greater than 100 ppm deal with a polymerized phthalate present in the composition of nitrocellulose paint through phthalate plasticizers or alkyd resin ($\delta^{13}\text{C} = 167\text{ppm}$). Nitrocellulose can also be found in the HSQC spectrum (in negative by the pairs $\delta^{13}\text{C}-^1\text{H}$ (ppm)): 68-3.65; 68-4.2; 66-3.5 and 65-4.35 [26] and also detected in the ^{13}C spectrum (Figure B.2). Those results are also in good agreement to previous results published by Mejia-Gonzalez on plasticized nitrocellulose [26].

Finer information and better signal detection could be obtained using larger magnetic field, helping with the gain of signal/noise ratio and allowing to show certain missing correlations on the 2D coupling spectra.

In conclusion, for the MS733 sample, FTIR allowed to identify nitrocellulose resin and thanks to Py-GC-MS and NMR techniques, the presence of plasticisers DEEP and DEHP was confirmed. The presence of alkyd resin is yet to be demonstrated.

4.2.2. Identification of the organic binder on the rest of the corpus

Then, FTIR was used to analyse samples from the corpus that were classified by nationality. Except for samples LOP38, HE111 and HE177, the layers could not be separated in most cases and were analysed as a single sample. The black and yellow layers of LOP38 were both analysed. On HE111, the primer, second and fourth layers (see table 1) were separately analysed whereas only the red layer of HE177 was analysed.

Figure 3 shows the FTIR transmission spectra of the paint samples from a) German aircraft, b) American aircraft, c) French aircraft and d) Italian aircraft.

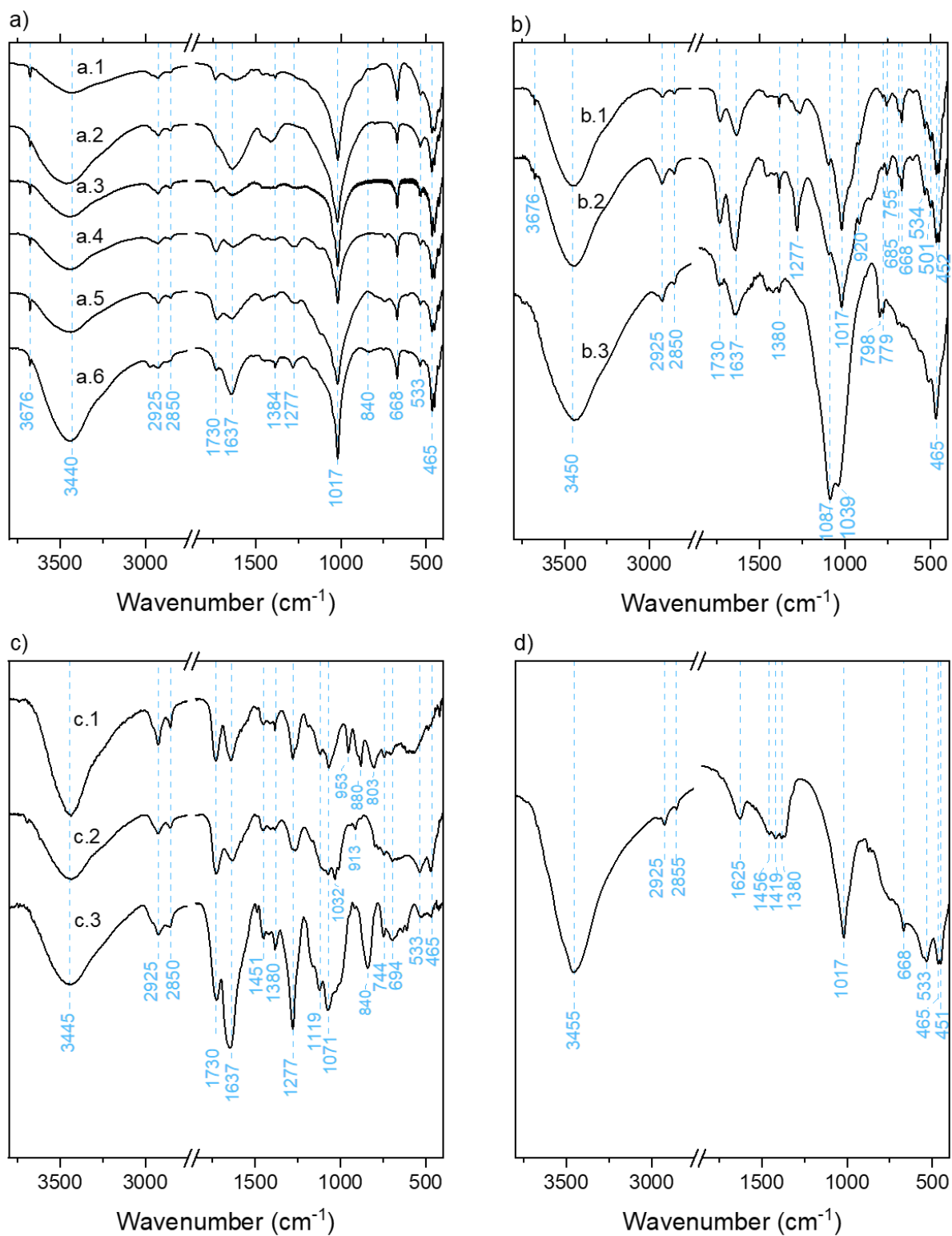


Figure 3. FTIR transmission spectra (arbitrary units on the Y-axis) of paint of a) German aircraft: a.1) JU88 ; a.2) HE111 – primer ; a.3) HE111 – layer 2 ; a.4) HE111 – layer 4 ; a.5) DO217 ; a.6) HE177 ; b) American aircraft: b.1) LOP38 – layer 3 ; b.2) LOP38 – layer 2 ; b.3) RAP47D ; c) French aircraft: c.1) DE520 ; c.2) LA298 ; c.3) MS733 and d) Italian aircraft: MAMC202.

The signals near 3440, 2925 and 2850 cm^{-1} in each spectrum are attributed respectively to -OH, -CH and -CH₂ groups, similarly to the MS733 sample. The peaks at 1730 cm^{-1} and 1384 cm^{-1} could be associated with carbonyl group and CH bonding. Vibration band at 1637 cm^{-1} could represent nitro group vibration. Those at 1277 cm^{-1} and 840 cm^{-1} could both be attributed to O-NO₂ bonding. As a result, the main binder of German aircraft is most likely to be nitrocellulose-based. The identification of the binder, however, is less clear than in the MS733 case. Even though some characteristic vibration bands of nitrocellulose were observed, the signals of fillers outweighed organic components on FTIR spectra. The samples from German aircraft show indeed several well defined signals (Figure 3.a) that correspond to talc mineral filler [26] [32] and agree with previous analysis (XRD, Raman, SEM-EDS): the peaks at 3676 cm^{-1} and 465 cm^{-1} are attributed to stretching vibration of hydroxyl group in Mg(OH) bonding, the one at 668 cm^{-1} is attributed to Mg-O, and the ones at 1017 cm^{-1} and 533 cm^{-1} are attributed to Si-O vibration (in MgSiO structure).

Filler was also identified on the FTIR spectra collected on the samples from American aircraft. Bands at 1087, 798 and 779 cm^{-1} on the RAP47D paint spectrum are attributed to quartz [33](Figure 3.b.3). The peak at 1637 cm^{-1} could be related to a nitro group but because of the other quartz vibration bands detected, it is not possible to conclude on the presence of nitrocellulose in this sample. Signals at 3676, 1094, 1020, 920, 779, 755, 685, 668, 534, 501, 465, 452 and 427 cm^{-1} on the spectrum of the LOP38 paint (Figure 3.b.1 and b.2) are associated to anthophyllite filler [34] identified in previous section. The other signals indexed (3450, 2950, 2850, 1637, 1730, 1277, 1380 cm^{-1}) could indicate either nitrocellulose or alkyd resin /phthalate type plasticisers.

Regarding the French aircraft (Figure 3.c), peaks at 3445, 2925, 2850, 1730, 1637, 1380, 1277, 1119, 1071, 744 and 694 are common and are associated (as demonstrated in the MS733 case) with nitrocellulose and phthalate type plasticisers. The FTIR spectrum of the DE520 paint (Figure 3.c.1) then shows distinct spectral profiles with 953, 880 and 803 cm^{-1} vibration bands assigned to zinc chromate (4ZnCrO₄·K₂O·3H₂O) [35], the corrosion inhibitive pigment already detected in the primer by SEM-EDS. Vibration bands at 533 and 465 cm^{-1} on the MS733 paint spectrum (Figure 3.c.3) and on the LA298 paint spectrum (Figure 3.c.2) may be associated with an unidentified filler or a pigment (there is not enough other bands to conclude).

Talc filler was identified in the spectrum of the Italian Macchi paint in the same way that it was found in the German aircraft paint (except for the peaks 3676 cm^{-1} and 424 cm^{-1}). The remaining vibration bands are insufficient to provide a clear conclusion. One hypothesis is that nitrocellulose is damaged, but it could also be another binder. The paint of the Macchi is very powdery in both cases, which is a sign of ageing: the binder is most probably very degraded. Furthermore, the paint is mixed with corrosion products in its current state making identification even more difficult.

5. Discussion

By analysing the different samples of the corpus, common features and differences between constructors within each nation can be highlighted and discussed.

Although different colours of paint were used on German aircraft, their compositions were quite similar among the various constructors: Heinkel, Dornier and Junkers. Talc was widely employed as a filler. Anatase, barite or zincite were found as white pigments. Lead chromate was also found as a yellow pigment. However, differences in inhibitive pigments can be reported in the primers. As much as three inhibitive corrosion pigments were identified: zinc chromate (JU88), zinc potassium tetroxochromate (HE177) and lead chromate (HE111). It can be concluded that the choice of primer was left to the constructor. Regarding the organic binders of German aircraft's paint, nitrocellulose plasticized with alkyd resin and/or phthalates was identified. We know from ancient literature that nitrocellulose and oil-modified alkyd resin were widely used in paint for thin and large aluminium pieces during WWII [16, 36]. Other binders include phenol-formaldehydes [10, 15, 37]. However, no phenol-formaldehyde resin was discovered in the recovered German painted samples contrary to what was recently reported by La Nasa et. al [38] on the same period's aircraft paint (Messerschmitt Bf1109) and despite the fact that these products (AlbertolTM) were known to be used for metal aircraft during World War II [15].

The paint system for the two older French aircraft (Dewoitine 520 and Latécoère 298, both from 1940) was a red primer over which the paint was applied (with the adapted colour chosen by the constructor). The Morane Saulnier 733 aircraft (from 1951) has a unique primer: a very thin green layer containing zinc chromate and phosphorus which could correspond to a wash primer. Wash primers are film-forming products that provide active phosphoric and chromic ions with potential reactivity [30]. Two products are mixed: one based on vinyl butyral resin, pigmented with zinc tetroxochromate. The other is an alcoholic solution of phosphoric acid. The mixture reacts on the surface of the aluminium producing a phospho-chromo-resin compound. The difference demonstrates how corrosion protection technology evolved during and after WWII. In terms of organic compounds, the three French aircraft paints are based on nitrocellulose resin mixed with plasticisers. Surprisingly, the later aircraft Morane Saulnier 733 conserve the same organic binder as the WWII aircraft, although more resistant binders had been developed in the meantime (alkyd resins and polyurethane). The widespread use of nitrocellulose resin as a binder in German and French aircraft is most likely related to the product's industrial history. Nitrocellulose was indeed originally used in the production of explosives, and large stocks of this product remained available shortly after World War I. Industrials developed paints and varnishes based on nitrocellulose to take advantage of the leftovers [37].

One of the identified fillers for American aircraft is a magnesium-silicate compound in the paint applied to the blade of the Lockheed P38 Lightning. The grain size of the filler is coarser than on other aircraft. It could be linked to this specific part (blade), a forged product for which paint serves more as a protective layer than a colouring layer. On either American aircraft, the identification of the organic binder was not possible due to the overlapping of the fillers (quartz and anthophyllite) in the FTIR spectra and/or possible alteration related to the long stay in the sea (for the P-47D Thunderbolt). In old literature, various products are reported: in early days, petroleum-based products such as CosmolineTM or ParalketoneTM [39] and from 1943, EronelTM (a cellulose butyrate acetate plastic) and PlastiphaneTM (a vinylite-based resin)

[40]. Certain binders were restricted to military use in the United States during WWII, as reported in [10] and in the report of the NACA from 1939 [41]: phenol-formaldehydes (so-called Thresher™ varnish or Bakelite Marine spar varnish), alkyds (Glyceryl phthalate, from the Dulux brand name) and vinylites. These binders were an alternative to the nitrocellulose-based paints.

The state of conservation of the remains on the Italian aircraft (sample MAMC202), did not allow to draw clear conclusions, particularly on organic compounds, once again due to the alteration/ageing in the landfill.

It is interesting to point out that all the aircraft before 1940, whether French (DE520, LA298) or German (JU88) were using the above-mentioned red primer including hematite and chromate species. Although no American aircraft from this period was studied, it is known that a paint with iron oxide and zinc chromate was also developed by the Bureau of Aeronautics of the Navy Department (USA) [8]. This red primer is thus a chronological marker of pre-war protection technology although interpretation should always be cautiously made especially for French aircraft: the French aeronautical industries were late to catch up after WWII. Consequently, some pre-war technologies could still be employed on more recent aircraft.

6. Conclusions

In conclusion, the multi-analytical techniques approach enabled the identification of mineral compounds (pigments, fillers) as well as the principal organic binders of paints and primers originated from various WWII aircraft wrecks.

SEM-EDS analyses combined with XRD and Raman spectroscopy brought new and informative data on mineral compounds and their use by constructors of various countries. Common techniques, such as the use of talc as a paint filler in Germany, but also in Italy, coexisted. White pigments included titanium oxide (mostly anatase, but rutile was also found), barium sulphate (barite), zinc oxide (zincite) and lithophone. Antimony oxide was detected in only one sample, collected on a German aircraft. In most aircraft, yellow pigment was lead chromate (crocoite) and red pigment was iron oxide (hematite). Blue pigments were not yet identified. Corrosion inhibitive pigments based on chromates were either zinc-potassium tetroxychromate (in France and Germany) or zinc chromate (in USA). Lead chromate could also play this role. On the most recent aircraft Morane-Saulnier MS733 (1951), a different primer was applied, more likely a wash primer, evidencing the evolution of the technology in this field.

In terms of organic components of the paints, we confirm thanks to the combination of FTIR, Py-GC-MS and NMR methods that nitrocellulose is the main binder of the paint layers of MS733, plasticized with phthalates compounds (DEEP and DEHP). The presence of alkyd resin, often used as a plasticizer for nitrocellulose paint, is however uncertain and remains to be established. On other aircraft, the paint binders were identified through comparison with MS733 although various factors such as ageing causing binder degradation or forming mixtures with corrosion products and the presence of inorganic compounds made identification more difficult. It was shown that all French aircraft and most probably all

German aircraft, used the same paint system based on nitrocellulose binder. However, on the American aircraft, constructors appear to have applied different binders from other countries. These binders are yet to be identified. A thorough research in archives is needed to fully comprehend these paintings and connect historical data with the identification of these ancient materials.

This work is a first step toward a better understanding of the painting systems applied on aircraft by various countries during a specific historical period. It will guide future intervention considered in the PROCRAFT project, particularly protective coatings.

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