Periodico di Mineralogia (2015), 84, 3A (Special Issue), 483-495 DOI: 10.2451/2015PM0027

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on Environment, Archaeometry and Cultural Heritage

White zinc in linseed oil paintings: chemical, mechanical and aesthetic aspects

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Abstract

The interest of this research derived from the request for a scientific investigation of the observed phenomenon from a few contemporary artists who, in some occasions, observed the formation of craquelure in pentimento areas where a paint layer of different colour was over imposed to a zinc white layer, on commercial canvases. To investigate this phenomenon several investigations to characterize chemical and physical properties of commercial white zinc pigments were carried out: XRD, ICP/OES, SEM/EDS, FTIR, GC-MS. Moreover, several tests were performed in order to show the different behaviour of the various white pigments referring to the miscibility and to the drying times. This paper shows how the size of the pigment particles affect the formation and the type of the craquelure.

Key words: White of zinc; craquelure; oil painting; commercial pigments; analytic investigations.

Introduction

White of Zinc is a pigment commonly present in oil paintings both alone and in mixtures with white of titanium dioxide (Auer et al., 2005). Although the use of this pigment has a long history and has been widely adopted, some of its characteristics have been known for certain risk factor on the surface of the painting. It is well known that the fragility of the pictorial layer obtained with this pigment causes the formation of craquelure even shortly after the time of its application. Well known is the case of the Dutch artist Han Van Meegeren, who realized his faults and aged them, mixing a small amount of zinc white in the pigment.

The interest of this research derived from the request for a scientific investigation of the observed phenomenon from a few contemporary artists who, in some occasions, observed the formation of craquelure in pentimento areas where a paint layer of different colour was over imposed to a zinc white layer, on commercial canvases. The formation of craquelure and their typology generally resulted to be influenced by the producer of the pigment. The present study is therefore focused both on the application technique and the analytical study of the pigment employed.

The reaction responsible for the formation of craquelure, in fact, has not yet been completely understood. Probably, it starts from the formation of hydroxide (Pappas et al, 1974) or superoxide (Daniels, 1990) radicals on the surface of the pigment due to the interaction among the pigment particles, or to the atmospheric humidity, oxygen and UV light influence. The produced chemical species are able to deteriorate the oil binder. Reactions due to zinc oxide are still object of studies and appear largely dependent on the purity degree and particle size. These phenomena are typical of white of zinc used to perform the pictorial layer, but the artists denounce the formation of craquelure also in the case of using white of zinc as basis layer for the another pigment. The evidence of craquelure can derive from the "modus operandi" of the artists, sometimes wanted and/or from the micro clime or other chemical - physical mechanisms. Which is the right answer? What is the importance of the particle size? It is also confirmed that zinc oxide produced according to the French process is generally characterized by micro particles tiny and morphologically colloidal enough to form a more extensive film tending to be more sensitive and subject to alternative mechanisms such as cracking. Particularly, as reported by Morgans (Morgans, 1982), the size of the particles seems to promote the production of craquelures, especially those of nodular look. In order to confirm this hypothesis, the formation of craquelure on overlying pigment on white of zinc layers was studied. To this aim, organic and inorganic components of some commercial pigments have been analysed in order to define analogies or differences and eventual problems related to their use in combination with other pigments. The chemical characterization was necessary because to lack of technical sheets of the pigments.

Materials e methods

Pigments

To realize the pictorial layers, commercial pigments suggested by the artists have been employed. They are listed in Table 1.

Experimental

Analysis. The sample of Table I where analyzed by different techniques:

X-Ray Diffraction - XRD: to identify

Table 1. Pigments used in the research.

	Name of Product	Colour	Name used in this paper
1	Maimeri Artisti 20 ml (1)	White	A
2	Maimeri Artisti 20 ml (2)	White	B
3	Le Franc fine	White	C
4	Mussini 35 ml	White	D
5	Le Franc extra fine	White	E
6	Maimeri Artisti gr.1	White	F
7	Ivory black Maimeri	Black	G
8	Ivory black Mussini	Black	H
9	Ivory black Lefranc	Black	I

Note: (1) = New; (2) = given by Artists

crystalline compounds. The spectra were recorded on powders after their treatment in oven at 600 °C for 6 hours (hrs) in order to eliminate the organic part. The residue was grinded and analyzed by CuKα1/Ni radiation at 40kV-30mA with scanning rate: 1 min.

Inductively Coupled Plasma Optical Emission Spectroscopy - ICP/OES (Varian VISTA-MPX CCD SIMULTANEOUS ICP-OES) to determine the elemental composition referred also to the trace elements and to the elements associated to the primary element of the pigment, i.e. Zinc (Zn). The samples were heated and (instrument: Mars 3) the residue was mineralized by microwave digestion system using aqueous nitric acid + hydrogen peroxide mixture at 90 °C (HNO_3 (65%) : H_2O_2 (35%) : H_2O = 5:3:2).The results of ICP are given as % by weight of the found elements.

Scanning Electron Microscope and Energy Dispersive X-Ray Spectrometer - SEM/EDS [SEM EVO 50 XVP (Carl-Zeiss Electron Microscopy Group) - INCA Oxford Energy 400]. This test was needed due to the presence of a residue in the mineralization process used for ICP/OES analysis. Elemental analysis on the calcined pigments was compared with that one on the pigments with the aim of pointing out eventual anomalies due to the treatment of these pigments.

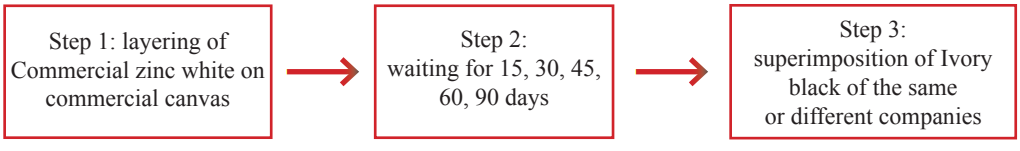
Fourier Transform Infrared (FTIR) Spectroscopy: applied to detect functional groups present in the organic component. This test was performed on extracts by soxhlet apparatus with isopropylic alcohol. A thin layer of the samples were deposited on CsI windows and the absorbance spectra studied in the range 4000 - 400 cm^{-1} at a resolution of 1 cm^{-1} cumulating at least 200 scans using a Bruker Interferometre IFS 113 v under vacuum.

Pyrolysis gas chromatography Mass spectrometry (Py-GCMS) Perkin Elmer Clarus 500 with pyrolyser SGE II to study the thermal stability and analyse relatively high molecular weight compounds.

Tests a) Tests on overdose pictorial layers. Several tests were performed in order to evidence the different behaviour of the various white pigments referring to the miscibility and to the drying times. Different specimens were realized (2.5 x 2.5 cm) layering on commercial canvas one of the zinc oxide pigments reported in Table 1. After different intervals of time (15, 30, 45, 60, 90 days) a layer of ivory black pigment produced by the same or different company was superimposed. The tests involved all the white pigments and were repeated at least three times. All specimens were protected from solar light during the drying phase. A specimen was left as such as reference. The process is summarized in Scheme 1.

b) Measurements of the thickness of the pictorial layers

To determine the influence of the pictorial layer thickness on the craquelure formation, some tests were performed on layers of Maimeri and Le Franc layers of different thickness: fine, mean, great. After 30 days, the black pigment of the same company was applied. The measurement of thickness was realized by sampling specimens on painted



Scheme 1. Preparation of samples for tests on overdose pictorial layers.

stuff, immobilized in epoxy resin, crosswise cut and observed using optical microscopy at 100 magnitude value.

c) Study of craquelure

The study was obtained by imaging acquisition of every specimen and elaboration using Adobe Photoshop software. To quantify the entity of the craquelure, the ratio % among altered and non altered areas was performed applying Autocad 2008 to the acquired image of all the specimens and approximating the craquelure to rectangles.

Morphological analysis by SEM. Morphology of the particles in the two pigments black showing more and less amounts of craquelure, was analyzed by SEM in order to evaluates size, shape and dispersion of the particles. These parameters are very useful to the comprehension of the capacity of binder to wet the pigment but do not allow a definition of the critical volume concentration of the pigment (CVCP). For this analysis, the pigments, after extraction of the organic component, were dipped into epoxide resin and analysed after metallization.

Table 2. XRD Analysis of different zinc white used in the experimentation.

	Zincite	anatase	quartz
Maimeri Artisti 20 ml (1)	++++		++
Maimeri Artisti 20 ml (2)	++++		++
Le Franc fine	++++		
Mussini 35 ml	+++	+	+++
Lefranc extra fine	++++		+
Maimeri Artisti gr.1	++++		

References: Zincite:z 36-1451; Anatase (RRUFF ID: R070582.9); Quartz (RRUFF ID: R060604.1).

Gas chromatography/ Mass spectrometry (GC-MS). GC-MS was used to determine the Content Percentage of unsaturated fatty acids responsible for the drying process. To prepare the sample to be analyzed by GC-MS, oil was extracted from 3 grams of pigment by a mixture of acetone and methanol (7:3 v/v) and saponified by a 10% KOH (w/v) solution. The produced fats were derivatized and transformed into their methylesters by a transesterification reaction and extracted by methylene chloride. GS-MS analysis was performed by a Thermo Quest GC-8000 equipped with a Supelco 30 m x 0.25 mm column, film thickness 0.5 μm interfaced with a MD-800 Spectrometer. Injection temperature 300 °C, while at the interface of MS it was 270 °C. Analysis was performed according to experience details reported in literature (Sutherland K, 2001). Temperature program was established from 120 °C to 300 °C with a rate of 10 °C / min.

Results & Discussion

Results of analysis

X-ray diffractometry. Analyzed pigments (Table 2) showed a very similar mineralogical composition among them, characterized by the prevalent present of ZnO. Quartz, present in some pigments, and TiO_2, present in Mussini, are substances added to give to the pigment different optical and mechanical properties. Chemically, their low amount does not affect the reactions that depends solely on zinc white.

ICP Spectroscopy. ICP/OES was performed in order to check the presence of trace metals. The percentage of the trace elements found in the examined samples respectively Ca, K, Ba was lower than 1% = ppb order (Table 3).

The presence of a residue after the mineralization process requires a more detailed investigation of the elements constituting the pigments by SEM/EDS. At this aim, pigments

Table 3. ICP/OES Analysis of pigments.

	Weight of the calcined pigment (mg)	% residue after mineralization	% Ba	% Ca	% K	% Ti	% Zn
Maimeri Artisti 20 ml (1)	121.2	6.0%	-	-	-	-	87.5
Maimeri Artisti 20 ml (2)	120.1	6.0%	-	-	-	-	88.0
LeFranc fine	130.2	1.0%	-	-	-	-	88.8
Mussini 35 ml	132.2	16.0%	-	-	-	3.7	81.7
Lefranc extra fine	123.5	6.0%	-	-	-	-	92.3
Maimeri Artisti gr. 1	122.0	1.0%	-	-	-	-	84.5

Table 4. SEM/EDS Analysis of pigments.

	% Elements			
Product	O	Si	Ti	Zn
Artisti 20 ml (1)	14.34	0.54	-	85.12
Artisti 20 ml (2)	14.60	0.67	-	84.73
LeFranc fine	14.67	1.60	-	83.73
Mussini 35 ml	21.19	2.53	3.41	72.87
Lefranc extra fine	15.18	0.44	-	84.38
artisti gr. 1	13.89	0.24	-	85.87

Table 5. SEM/EDS Analysis on the different pigments directly applied on SEM graphite supports.

	% Elements			
Product	O	Si	Ti	Zn
Artisti 20 ml (1)	30.84	0.86	-	68.31
Artisti 20 ml (2)	30.15	1.01	-	68.85
Lefranc fine	25.11	1.23	-	73.66
Mussini 35 ml	30.14	3.05	4.43	61.38
LeFranc extra fine	31.12	0.56	-	68.38
artisti gr. 1	33.86	0.85	-	65.29

were calcined and homogenized in agate mortar. The results listed in Table 4 are expressed as weight relative percentage.

Furthermore, the pigment layers were directly examined as such by SEM/EDS with the aim to point out eventual anomalies due to paint. Samples before EDS analysis were dried at 60 °C in oven for 7 days. Data are reported in percentage by weight and normalized by eliminating carbon (Table 5). The results confirmed the prevailing presence of zinc and confirm that the residue of ICP/OES pre-treatment is SiO_2

Le Franc Fine pigment showed a SiO_2 amount higher than that one obtained by mineralization. This result, considering the absence of aluminum (Al) as index of silicate presence, has to be assigned to a greater efficacy to the solving process in comparison with other pigments.

FTIR Analysis. FTIR spectra of the different pigment samples (Figure1) can be compared to a linseed oil standard in order to define this compound as binder in all the used pigments.

FT IR absorption bands and functional groups detected in the spectra are collected in Table 6. The observed bands are assigned according to literature data (Lazzari and Chiantore, 1999;

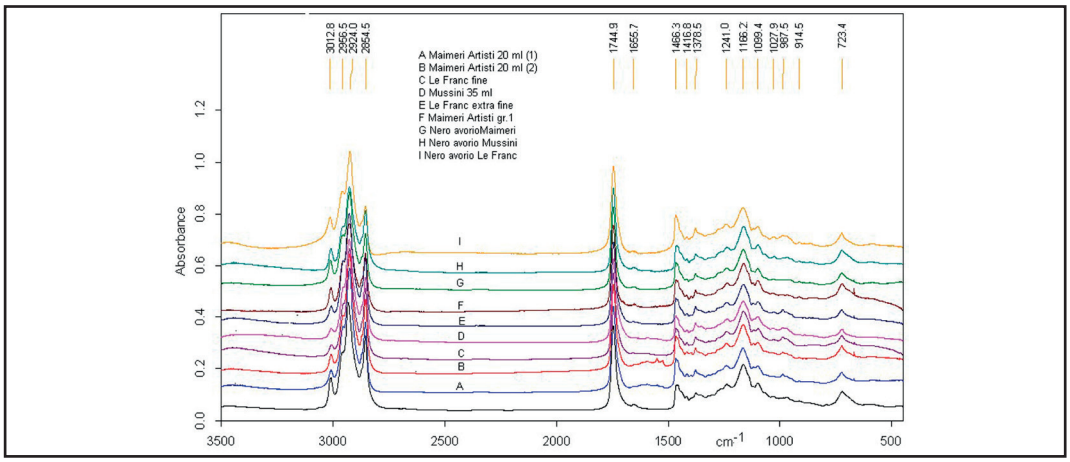


Figure 1. FTIR spectra of white (A-F) and black pigments (G-I). For comparison, the infrared spectrum of linseed oil is also reported

Table 6. Infrared absorption bands (cm^{-1}) of linseed oil and Soxhlet extracted samples and proposed assignment.

Frequency (cm^{-1})	Proposed assignment
3012.8 m	ν(C-H)=C-H
2956.5 ms	ν_a(C-H) CH_3
2924.0 s	ν_a(C-H) CH_2
2854.5 ms	ν_s(C-H) CH_2
1744.9 s	ν(C=O)
1655.7 w	ν(C=C)
1466.3 m	δ(CH_3)
1416.8 w	wag (CH_2) CH_2- CO-O-
1378.5 mw	wag (CH_3)
1241.0 m, br	ν_a(C-C-O)
1166.2 m	ν(C–O)
1099.4 mw	ν_a(O- CH_2-C)
987.5 w, br	Trans-trans conjugated double bond
914 5 vw	Trans-cis conjugated double bond
723.4 mw	γ $(CH_2)_n$- wag (C-H)=C-H

Mallegol et al., 2000). The spectra of Soxhlet extracted samples seem to reproduce the spectroscopic behaviour of pure linseed oil. Sample B, however shows a very weak doublet at 1552.7/ 1527.0 cm^{-1} whose assignment would require further analysis. In addition, the peak at 987.5 appears more intense in soxhlet extracted samples with respect the same bands of pure oil suggesting an increased polymerization.

Results of application tests

a) Pictorial layers

Zinc white of the different companies was uniformly applied to the support at time interval from 10 to 90 days (Scheme 1) covered by a pictorial layer obtained with an ivory black pigment of the all companies used in the experiments. Figure 2 shows some phases of experimentation.

The test has evidenced:

In all the applications craquelures are formed.

The drying time of Le Franc extra fine zinc white is longer in comparison with the products from the other companies, which have comparable drying time.

The results show that the formation of craquelure is possible when an overlapping of a

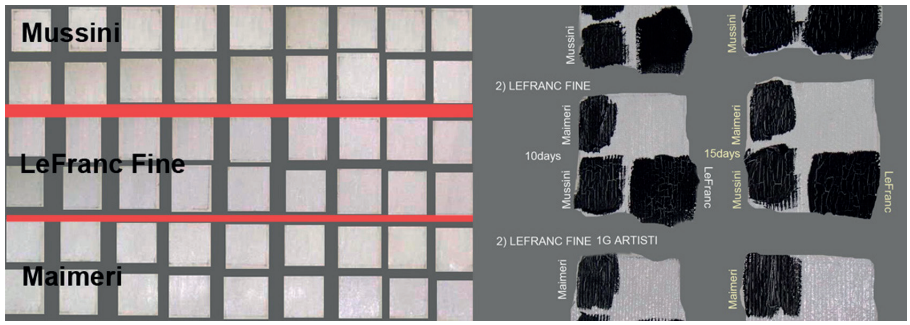


Figure 2. Specimens of white and application of black layer then 15 days (macro).

Table 7. Test to evaluate the influence of the pictoric layer thickness.

		Size (micron)			Craquelure Formation
		Maimeri	Le Franc	Mussini	
Fine	Preparation layer	15.0 ± 5.2	12.4 ± 5.4	19.5 ± 6.1	YES
	Pictoric layer	19.3 ± 5.8	9.3 ± 3.5	17.6± 4.3	YES
Mean	Preparation layer	22.9 ± 5.4	27.4 ± 2.1	25.1± 3.3	YES
	Pictoric layer	42.2 ± 4.7	54.4 ± 6.3	33.0 ± 3.6	YES
Great	Preparation layer	30.1 ± 3.4	22.6 ± 2.3	13.6 ± 3.5	YES
	Pictoric layer	69.2 ± 2.5	78.1 ± 1.3	66.8 ± 1.9	YES

pictorial layer to a zinc white layer is performed as in the case of ripensamento or intentional preparation of the stuff by artist.

b) Thickness of the pictorial layer

Data reported in Table 7 show that the formation of craquelure is not depending on the thickness values realize both the preparation layer and the pictorial one.

c) Study of craquelure

In the following, the results of the study of the craquelure are synthetized.

Figure 3 shows the type of craquelures observed, that is net shaped (Figure 3a) and vertical shaped (Figure 3b).

For each white pigment, the ratio between the areas with the craquelure (ac) and the total area (at) was quantified considering both the different drying of zinc white layer and the used different ivory black pigments. The calculation of the ratio ac/at was performed by Autocad 2008 software.

The results point out the formation of craquelure for all the monitored times (Figure 4). In all cases the craquelures number becomes

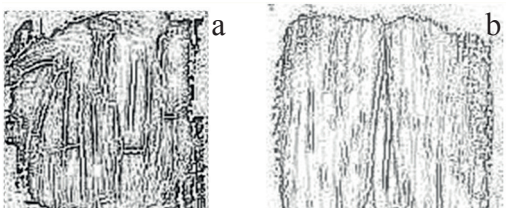


Figure 3. Type of the craqualure found during the research: net shaped (A) and vertical shaped (B).

Table 8. Size of Particles in the Le Franc Fine and Maimeri Artsti pigments.

Le Franc Fine	376.2 - 440.8 nm
Maimeri Artisti	249.9 - 346.9 nm

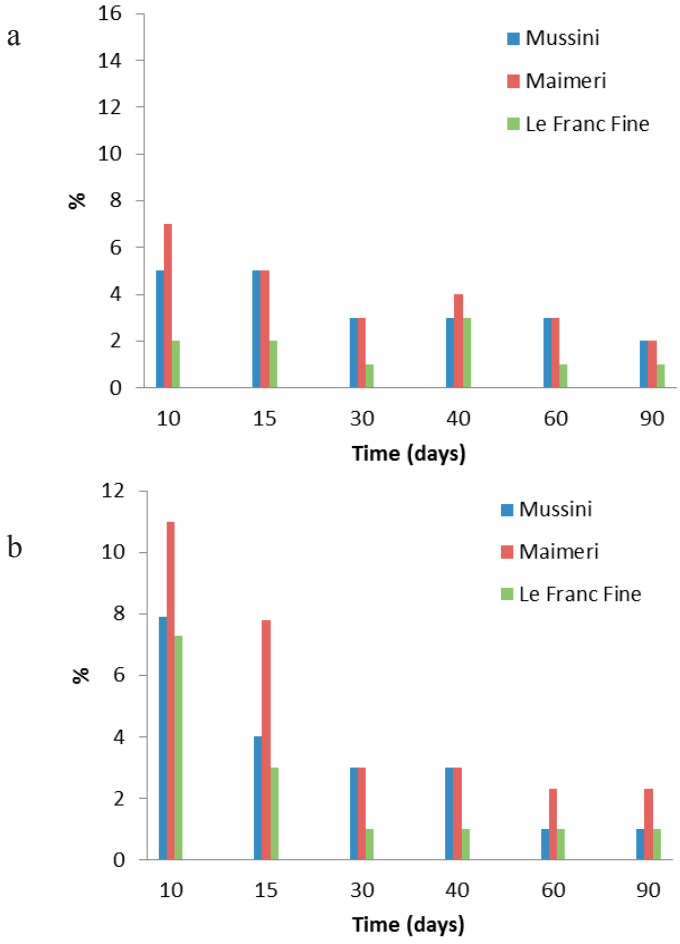
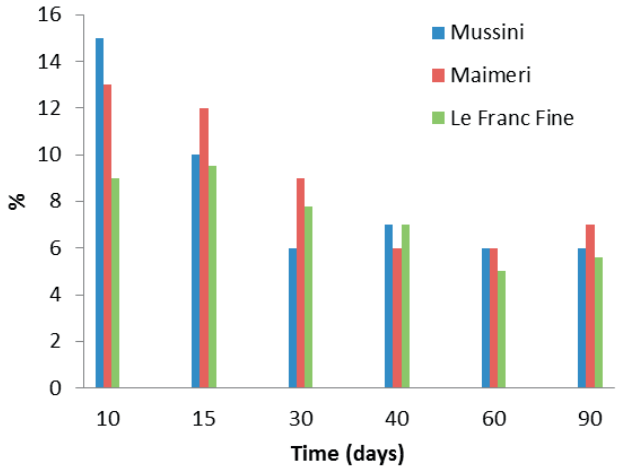


Figure 4. Monitoring of craquelure (ratio % ac/at) formed by superimposition of Mussini, Maimeri, Le Franc black ivory on a) Mussini zinc white; b) Franc zinc white; c) Maimeri zinc white (1g -Artisti) ; d) Maimeri zinc white (0.20 ml -Artisti); e) Le franc extra fine zinc white. In the first 45 days, black layer mixed itself with the white.

c



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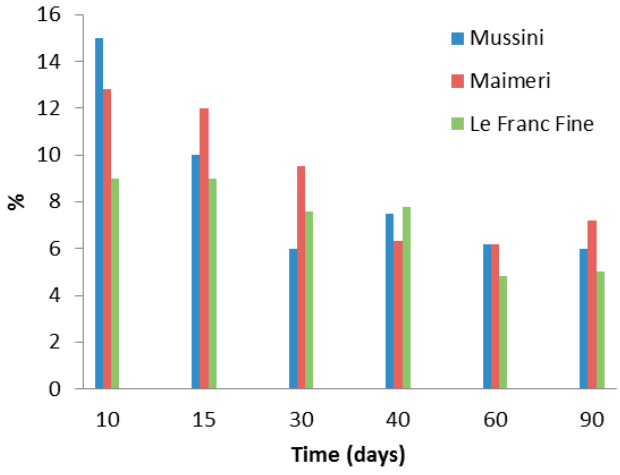

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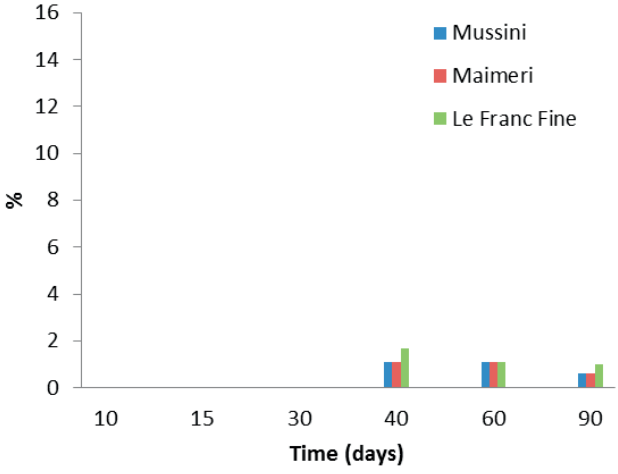

Figure 4. Continued...

lower if the inferior layer of zinc white is left to dry for more days (to confirm this hypothesis another test was realized). Some specimens of all white zinc were dried in oven at 60 °C for 30 days and then the back layer was applied. In all cases, craquelature was formed. The zinc white pigment produced by Maimeri shows the greater diffusion of craquelure both in the 1 g product and in the 20 ml. Le Franc extra fine white, although not completely dried even after 30 days, in the following experiments has shown the least craquelure formation.

To understand the different behaviour of mentioned pigments they were analyzed by SEM in order to determine morphology and size of their particles.

SEM

SEM analysis allowed to define the morphology and the size of the ZnO particles. Images obtained at different magnification for the two pigments are reported in Figure 5a and 5b and in Table 8 the dimensions range, anyway reported also in photo, is given.

The analysis of the images can be useful to investigate the relationship between the dimension of the particles and their adhesive power. The Maimeri product consists of very little particles which tend to constitute an homogeneous phase with the support which unlikely adheres to other pictorial layers. In contrast, greater particles and consequently less coherent can more easily immobilize superimposed layers.

GC-MS

Chromatographic analysis with MS detector has confirmed that the binder is linseed oil (Table 9 and Figure 7). In Figure 6 the differences of % fat acids in the oil of the pigments are reported. Data shows a greater content of linoleic acid in comparison with linolenic for the pigment Le Franc corresponding to a less drying power of the oil.

The experiments were carried out by Py–GC–MS. The SGE's Pyrojector II microfurnace pyrolyzer is interfaced to a PerkinElmer Clarus 500 gas chromatograph/mass spectrometer. Pyrolysis reactions take place in a quartz liner 130mm (in these conditions the time

Table 9. Products from the pyrolysis.

RT	m/z	name	formula
3.6	156	undecane	$C_{11}H_{24}$
4.38	154	1-octyn-3-ol, 4-ethyl	$C_{10}H_{18}O$
5.99	156		$C_{11}H_{24}$
8.77	184	tridecane	$C_{13}H_{28}$
11.5	198	tetradecane	$C_{14}H_{30}$
24.8	284	Hexadecanoic acid	$C_{18}H_{36}O_2$
27.85	308	Ethyl linoleate	$C_{19}H_{34}O_2$
27.96	310	Ethyl oleate	$C_{20}H_{36}O_2$
28.4	294		$C_{19}H_{34}O_2$
29.26	294	Octadecanoic acid methyl ester(Me-linoleate)	$C_{19}H_{34}O_2$

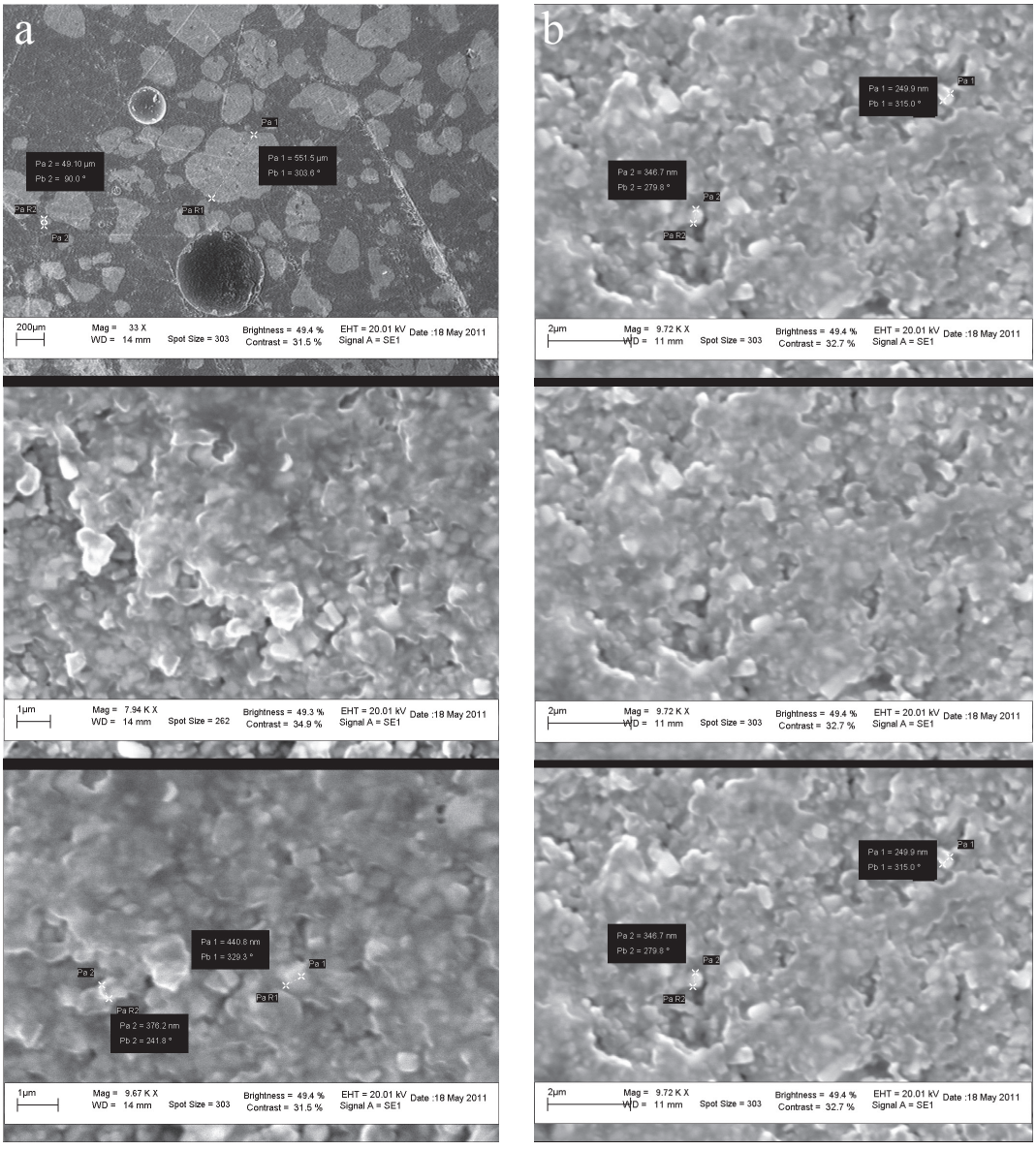

Figure 5. SEM analysis of white Le Franc Fine (left column, a) and white Maimeri Artisti (right, b).

of pyrolysis has been calculated ≈ 0.3 s). The pyrolysis products were separated on ValcoBond VB5, Valco Instrument Co. Inc. (30 m, id 0.25 mm), stationary phase 5% phenyl, 95% methylpolysiloxane capillary column.

Experimental results obtained suggests that the greatest formation of craquelure is observed in the case of Maimeri Zinc white. On the contrary, Le Franc extra fine pigment even if not completely dried after 30 days, showed the least

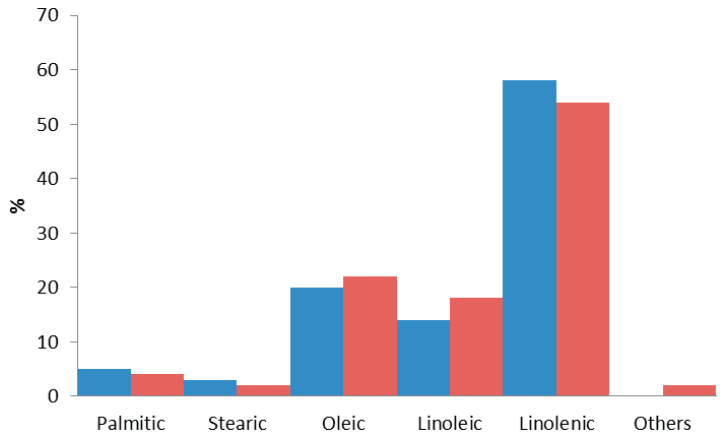

Figure 6. The % of fatty acids present in two pigments of zinc white: Maimeri Artisti e Le Franc Fine.

number of craquelure observed. For long drying times, considering the percentage reduction of craquelure during the time, Maimeri pigment is characterized by a lower number of craquelure in comparison to Le Franc one. The SEM experiments were very useful to correlate the size of the particles of the pigment which their effects on the adhesion of the overlapping layer. It is possible to hypothesize on the basis of SEM images that when, as in the case of Maimeri

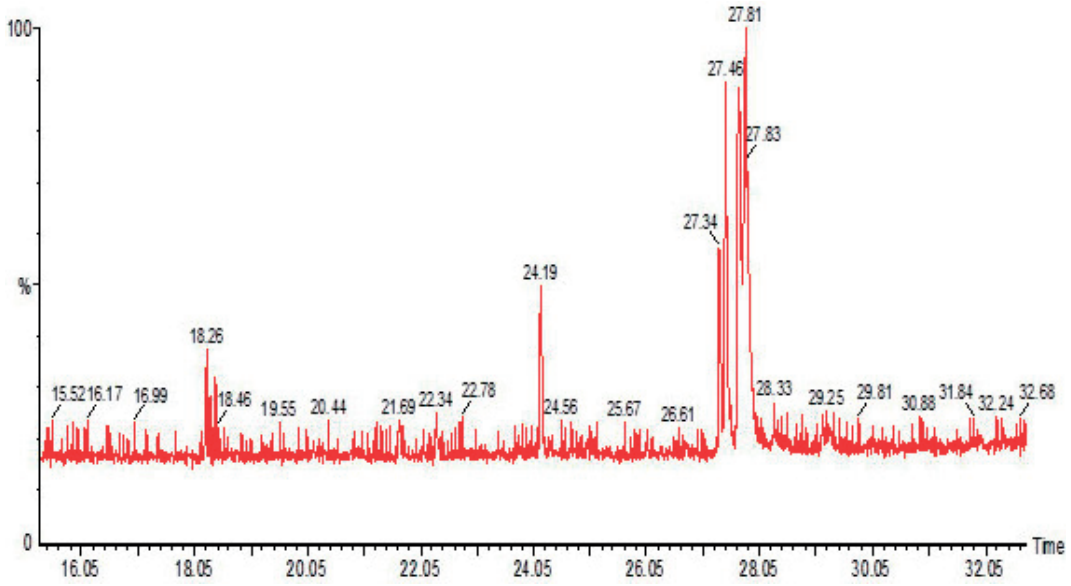

Figure 7. Pyrogram of Maimeri White Zinc at 500 °C.

product, these particles are very little (250.92 nm ± 3 nm) they tend to constitute a very short homogeneous phase but of difficult adhesion to the supporting material. On the contrary when the particles are greater and as such less coherent (Le Franc: 420.17 nm ± 37.37 nm) they show a greater capacity to immobilize materials of overlapping layers. Also the ratio between linolenic acid and binder can be another very meaningful index as the concentration of linoleic acid is inversely related to the drying capacity and it could affect the formation of craquelure. On the basis of this research, the different pigments show comparable behaviour depending on the producer. The size of the pigment particles affects the formation and the type of the craquelure.

Conclusions

Zinc white is a pigment used in oil painting alone or in mixture. Although it diffuses well it is considered responsible of craquelure obliging artists to look for better commercial products and to make request for research in the case of overlapped layers of different coloured pigments. Some commercial products have been tested with many independent techniques (ICP/OES, XRD, FTIR, GC-MS, SEM). The results obtained suggest that when the drying time is enough long (more than 90 days) the formation of the craquelure is much less on all the samples and particularly a comparable value among the different pigments of ZnO is obtained. The number and the shape of craquelure depends on the size of the zinc oxide particles dispersed in the medium.

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Submitted, February 2015 - Accepted, September 2015