

APRELIMINARY STUDY OF THE COMPOSITION OF COMMERCIAL OIL, ACRYLIC AND VINYL PAINTS AND THEIR BEHAVIOUR AFTER ACCELERATED AGEING CONDITIONS

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Keywords: contemporary paints, degradation, artificial ageing, preventive conservation

1. Introduction

Conservation, cleaning and general interventions on traditionally painted surfaces have a long history of practice and research. During this time there have been occasional setbacks, but also several exciting new developments. In contrast, diversity in the stability and transformations that industrial paints used in contemporary works of art are subject to with the passing of time have only recently been recognized as being distinct processes from those occurring in traditional paints [1 - 2].

Industrial development during the twentieth century has brought with it the rapid production and diffusion of synthetic binding media in industrial paints, leading to a radical change in the formulation of artists' materials [3]. Because of the complexity of these products, whose composition is often not completely known, it is possible their characteristics are affected over time, due to interactions between the media, pigments, additives and all the different enhancers used. As yet, in-depth studies in the behaviour of the resulting paint films have not yet been carried out [4 - 7].

Moreover, many contemporary artists in search of new visual effects, have been experimenting and mixing materials with different compositions and drying behaviour, in some cases compromising the durability of the artefacts themselves [8].

Recent studies and research have focused on studying the behaviour of these materials when subjected to different environmental conditions. The information thus obtained is typically related to degradation processes which have already affected the artworks [2, 8-10]. With the aim of promoting effective preventive conservation of contemporary paintings, we decided to test the stability of some industrial colours now available on the market and commonly used by artists.

Considering the huge choice of industrial paints available, a survey was launched among young Venetian artists and students from the Academy of Fine Arts to learn which are the most used. The survey found that nowadays the majority of artists prefer to use oil, acrylic and vinyl-based paints. The most widely used manufactured oil paints are Winton (Winsor & Newton, UK), for acrylic paints, Heavy Body (Liquitex, USA) and for vinyl paints Flashe (Lefranc & Bourgeois, France).

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For each product three commercial colours were selected based on their known reactivity and lightfastness: chromium oxide green (PG17), an inorganic pigment which appears to be quite stable in organic binding media; titanium white (PW6), the typical white pigment used in contemporary paintings, usually forming spongy films in oil media; the yellow azo-dyestuff (PY74) which is known to rapidly undergo fading and changes in shade under the influence of light [11 - 12].

2. Materials and methods

2.1 Preparation of paint samples

A full list of the selected paints is given in Table 1. The commercial name, brand, and product series, together with the declared composition in the manufacturer's catalogue are reported for each paint.

Table 1. Commercial description of the investigated industrial paints

Paint abbreviation *	Brand Product series	Commercial name and catalogue number (indicated formulation)
OG	Winsor & Newton Winton	Oxide of Chromium 31 (Anhydrous Chromium Oxide (PG17), pure Linseed Oil)
OW		Titanium White 40 (Titanium Dioxide (PW6), Zinc Oxide (PW4), Safflower Oil)
OY		Cadmium Lemon Hue (Arylide yellows) 7 (PY3-PY74 (Arylide Yellows), pure Linseed Oil)
AG	Liquitex Heavy Body	Chromium Oxide Green 166 (Anhydrous Chromium Sesquioxide (PG17), Acrylic Polymer Emulsion)
AW		Titanium White 432 (Titanium Dioxide (PW6), Acrylic Polymer Emulsion)
AY		Yellow Medium Azo 412 (Arylide Yellow 5GX (PY74 LF), Acrylic Polymer Emulsion)
VG	Lefranc & Bourgeois Flashe	Chromium Oxide Green 542 (PG17, Vinyl colour)
VW		White 001 (PW5-PW6, Vinyl colour)
VY		Senegal Yellow (primary) 195 (PY74, Vinyl colour)

* O=oil paint, A=acrylic paint, V=vinyl paint; G=green, W=white, Y=yellow

For each commercial paint, four sets of colours/paints were applied to inert glass slides 10×5 cm, coating them with a paint film 0.2-0.3 mm thick.

All prepared samples were left to dry at laboratory conditions ($25 \pm 1^\circ\text{C}$ and $60 \pm 3\%$ RH), which were constantly monitored with an Escort RH iLog® digital datalogger.

The curing period was fixed for all the paints at 80 days. This appears to be the appropriate length of time to ensure oxygen uptake for oil paints and the beginning of the drying process [11, 13].



Figure 1. Paint films with commercial formulation by W&N, Liquitex and Flashe

2.2 Artificial ageing

The artificial ageing treatments were performed using deliberately extreme ageing conditions in order to speed up the chemical reactions eventually involved in the curing of oil, acrylic and vinyl paints and their consequences on the morphological aspect of the film [14].

2.2.1. Exposure to ozone (O_3)

Ozone treatment was performed using a conventional industrial FISCHER ozone generator (*Labor-und Verfahrenstechnik Ozon-Generator*, Germany), with water cooling system, using oxygen gas as the raw material gas. The ozone is produced on demand in response to the amount of O_2 provided flue gas with a controlled ozone-oxygen ratio (1:5). The low operating temperature allows stable and constant control

regardless of variation in flow, load, or O₂ content. The samples were placed in a glass chamber on Teflon plates. The ozone concentration within the chamber was monitored using an Aeroqual S500 Monitor® ozone meter (0-1 ppm) equipped with Aeroqual Monitor Software.

The samples were exposed to O₃ for 8 hours and the average concentration of ozone was about 100 ppb, approximately 100 times higher than the recommended threshold value for the indoor conservation of organic artefacts [15].

2.2.2. Thermal ageing (T)

The paint films were thermally treated in air through heating in a laboratory oven at 100°C and 55% relative humidity (RH%) for 24 hours in the absence of light. Environmental conditions (T and RH%) were monitored with an Escort RH iLog® digital datalogger.

According to previous studies, these exposure conditions are strong enough to estimate degradation processes in close agreement with those obtained for naturally aged paint films [14, 16].

2.2.3. Treatment in environment with high level of RH

For the humidity treatment, all samples were exposed for 7 days at 20 ± 2°C in a sealed saturated salt chamber at 83% RH obtained using a saturated solution of potassium chloride as reported in the specific standards [17 - 18]. The relative humidity value inside the salt chamber was checked in conditions at equilibrium with an Escort RH iLog® datalogger and monitored during experimentation with conventional thermo-hygrometers.

2.3. Analytical techniques and instrumentation

Several complementary analytical techniques were used to investigate the composition (media, additives, pigments, extenders, etc) of the selected commercial formulations and to study their behaviour during drying and curing time, and after artificial ageing treatments.

Elemental analysis was performed using a Philips Minipal X-Ray Fluorescence spectrometer (XRF); the spectra collected were elaborated with Minipals software.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FT-IR) analyses were performed with a Thermo Nicolet FTIR NEXUS 750 instrument equipped with a Smart Endurance ATR diamond accessory, from 4000 to 400 cm⁻¹ and for 32 scans with a resolution of 4 cm⁻¹. Data were collected with Thermo Nicolet OMNIC 6.0a software and then elaborated with Origin 8 software [16, 19].

The Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC-MS) analysis was performed by using a Focus ISQ Thermo Quest Mass Spectrometer with a 20 meter SLB5ms column, id 0.18 mm, ft 0.18 µm; one-shot pyrolysis at 550°C. The inlet temperature was 300°C, while the MS interface was at 280°C. The temperature programme was set from 35°C to 300°C with a ramp of 10°C/min, held isothermally for 3 minutes; total runtime 25 minutes. The MS was run in Full Scan mode (m/z 40-600) with a speed of 1.9 scans/sec. Samples were derivatised with TMAH (tetramethyl am-

monium hydroxide) 2.5%, using tridecanoic acid as an internal standard. Data were processed using Xcalibur 1.4 software.

To monitor the mass variations occurring during the drying processes and the film formation of the paints, samples were weighed every day using a Mettler Toledo al204 analytical balance (precision 0.1 mg). All the investigated paint films were also weighed before and after each single ageing treatment to check for possible mass variations occurring with ozone, temperature and humidity cycles.

Colorimetric measurements were carried out on the paint films before and after ageing and performed with a Minolta CM-2600d/2500d colour spectrophotometer, in the 360-720 nm region in SCI (Spectral Component Included) modality. The L*a*b* colorimetric coordinates and ΔE (total colour difference) were calculated based on a D65 source of illumination and a 10° observer, using CIEL*a*b* 1976 colour space. Five measurements were carried out for each sample at different points (accurately identified with a mask) and the mean value calculated.

3. Results and discussion

3.1 Characterisation of the commercial paints

Table 2 reports the results obtained in terms of binders, pigments, additives, extenders, and fillers detected in the paint formulations with the joint use of several analytical techniques (XRF, ATR-FTIR and Py-GC-MS).

Table 2. Summary of the analytical results obtained for the analysed paints by XRF, ATR- FTIR and Py-GC-MS.

Paint samples		Composition of the paints			
Name	Brand	Pigment(s)	Extender(s)	Binder(s)	Additives
OG	Winsor & Newton (Winton)	chromium oxide green	calcium carbonate	linseed oil	metal soaps (likely aluminium stearate),
AG	Liquitex (Heavy Body)	chromium oxide green	/	acrylic emulsion (n-BA/ MMA)	plasticizers (dimethylphthalate), defoamers (silicon oils), stabilizers (dibutyl thiocarbamate, dimethylformamide)
VG	Lefranc & Bourgeois (Flashe)	chromium oxide green	calcium carbonate	vinyl emulsion (PVA-VeoVA)	dispersing and/or sequestering agents (polyphosphates)
OW	Winsor & Newton (Winton)	titanium oxide and zinc oxide	calcium carbonate	linseed oil and safflower oil	metal soaps (likely aluminium stearate), stabilizers (castor wax)

AW	Liquitex (Heavy Body)	titanium oxide	/	acrylic emulsion (n-BA/MMA)	plasticizers (dimethylphthalate), defoamers (silicon oils), stabilizers (dibutyl thiocarbamate, dimethylformamide)
VW	Lefranc & Bourgeois (Flashe)	titanium oxide	calcium carbonate	vinyl emulsion (PVA-VeoVA)	dispersing and/or sequestering agents (polyphosphates)
OY	Winsor & Newton (Winton)	Mixture of PY3-PY74	calcium carbonate	linseed oil	wetting agents (sulphonates), anionic surfactants, metal soaps (likely aluminium stearate), stabilizers (castor wax)
AY	Liquitex (Heavy Body)	PY74	/	acrylic emulsion (n-BA/MMA)	metal soaps (Cu, Ca, Fe metal soaps), plasticizers (dimethyl phthalate), defoamers (silicon oils), stabilizers (likely dibutyl thiocarbamate, dimethylformamide)
VY	Lefranc & Bourgeois (Flashe)	PY74	calcium carbonate	vinyl emulsion (PVA-VeoVA)	dispersing and/or sequestering agents (likely polyphosphates), plasticizers (diisooctyl phthalate) thickeners(colophony)

/=not detected

The Py-GC-MS analyses allowed the correct identification of the paint binding media [20 - 22]. Liquitex acrylic paints were analysed as co-polymeric emulsions of n-butyl acrylate and methyl methacrylate (n-BA/MMA), while a polyvinyl acetate/vinyl versatate (PVA/VeoVA) co-polymer is the main constituent of Flashe vinyl paints [23].

Based on the ratio palmitic acid to stearic acid (P/S) and the relative amount of specific fatty acids [9], Py-GC-MS results suggest that Winton oil paints are characterized by the presence of linseed oil in the OG and OY paints while a mixture of linseed and safflower oil is present as binder in the formulation of the OW paint.

Although no additives are indicated by manufacturers, chromatographic analysis underlined the presence of several organic additives, such as dispersing, sequestering, wetting, stabilizing agents and plasticizers (see Table 2). As an example, Figure 2 reports the m/z spectra of dibutyl thiocarbamate and diisooctyl phthalate respectively introduced as a stabilizer in the acrylic emulsion and as a plasticizer in the vinyl dispersion.

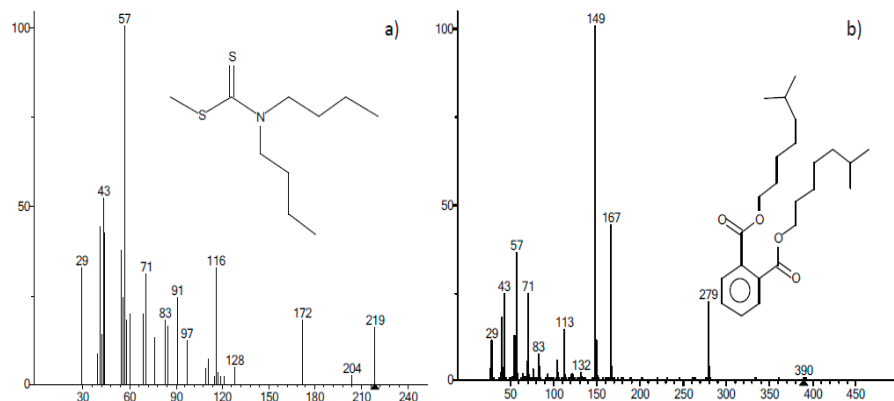


Figure 2. *m/z* spectra of (a) dibutyl thiocarbamate in the acrylic emulsions and (b) diisooctyl phthalate in the vinyl emulsions (as dimethyl esters after derivatisation and Py-GC-MS analysis)

Furthermore, the presence of hydrogenated castor oil (also called castor wax or 12-hydroxy stearic acid) was identified in the Winton yellow paint (OY), thanks to the identification of a specific marker (namely 12-hydroxy-octadecanoic acid). Castor wax is frequently added by manufacturers in commercial oil paint formulations as a rheology modifier and stabilising agent [24].

Elemental, inorganic and organic analyses of pigments confirmed what was declared by the paint-manufacturers. All green paints contain anhydrous chromium sesquioxide, commercially known as Chrome Green (PG17). Analysis outlined the use of a mixture of titanium white (TiO_2) and zinc oxide (ZnO) in the Winton white oil paint, while a mix of PY74 and PY3 was detected in the Winton yellow oil paint. Calcium carbonate was identified in all paints with the exception of the Liquitex acrylic paints, and was probably used as a filler in the paint formulations.

Besides the chemical composition, the mass variation percentage of the paint films caused by chemical-physical changes occurring during the curing and drying processes, were also monitored for the first 80 days after sample preparation (Figure 3).

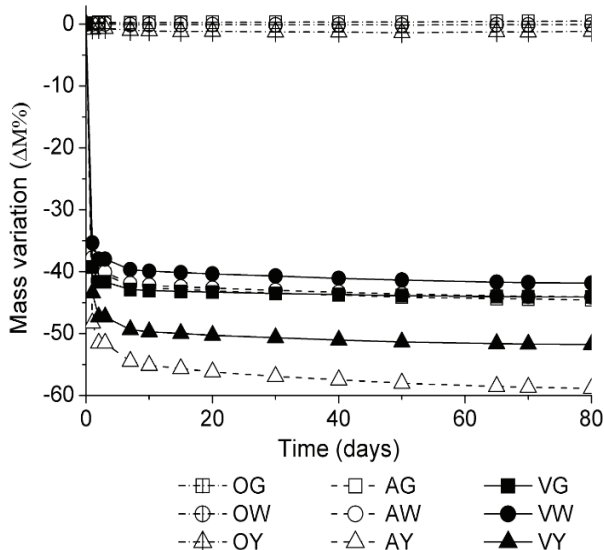


Figure 3. Winton oil (OG, OW, OY), Liquitex acrylic (AG, AW, AY) and Flashe vinyl (VG, VW, VY) paint films mass variation percentage ($\Delta M\%$) monitored during the first 80 days of natural curing

The resulting data are consistent with the known film-forming and drying properties of acrylic and vinyl paint [22, 25]. Vinyl and acrylic casting dispersion involves different steps: evaporation of the water fraction, deformation of the paint particles and the coalescence process with the final formation of a solid dried film [26]. As depicted in Figure 3, the Liquitex and Flashe colours showed a variation in mass during all the monitored curing period, primarily registered in correspondence to the very first days: this is mainly due to water evaporation from the emulsions. These variations were rather significant for the paints containing organic yellow dyestuff. Right after the first day, the Liquitex yellow paint (AY) presented a mass loss of 48%, while the Flashe yellow colour (VY) a loss of 43%.

Traditional oil-based paints usually exhibit an initial weight increase from oxygen uptake and then a mass loss due to the evaporation of volatile substances [27 - 28]. This trend, normally typical of unpigmented oil media, was not observed in the analyzed Winton oil paints since only a minor mass increase was recorded in the first days (Figure 2). The different behaviour in OW formulation might be explained due to the presence of safflower oil, whose drying behaviour differs with respect to traditional linseed oil. Another possible explanation might be linked to the addition of wetting agents, stabilizers, fillers, etc in the manufactured compositions [29 - 30], that might modify induction time and oxygen absorption.

3.2. Analysis of the paint films after ageing treatments

3.2.1 Exposure to ozone

Ozone treatment results in a general softening of all the paints, in particular for Winton oil paints.

After ozone treatment, the acrylic paints did not show any relevant chemical variations, while spectroscopic modifications were detected in varying degrees both for the vinyl and oil paints, mainly in correspondence with the binder absorption bands. Figure 4 shows the ATR-FTIR spectra obtained for the yellow paints OY, AY and VY subjected to ozone treatment.

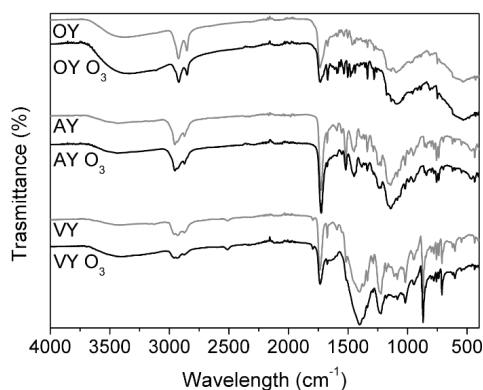


Figure 4. Comparison of yellow oil (OY), acrylic (AY) and vinyl (VY) paint films ATR-FTIR spectra before and after ozone treatments (OY_O3, AY_O3, VY_O3)

Being a strong oxidizing agent, ozone promotes the radical chain polymerization of oil, leading to the reaction of double C=C bonds and the cleavage of C=O bonds. This is evident in the Winton yellow paint (OY), whose FTIR profile shows a decrease in the intensity of the carbonyl absorption band at about 1735 cm^{-1} and of the CH stretching bands at 2920 cm^{-1} and 2850 cm^{-1} [16, 19, 31]. Moreover, after ozone treatment all the oil paints exhibit an FTIR absorption at around 1600-1700 cm^{-1} most likely due to the formation of oxidation products.

A higher degree of oxidation in oil paints after exposure to ozone was detected also by Py-GC-MS, as visible in Figure 5 which displays the pyrogram of Winton yellow oil (OY) paint after transesterification and chromatographic analysis. Besides the characteristic drying oil components (saturated fatty acids such as palmitic, stearic, myristic, lauric acids; unsaturated fatty acids such as oleic acid), several oxidation compounds due to the oxidative degradation of the original triglycerides were identified. They are mainly dicarboxylic acids (such as azelaic, suberic, sebacic, pimelic acids) and oxidised octadecanoic acid compounds (oxo-, epoxy-, dimethoxy-octadecanoic acids) [32].

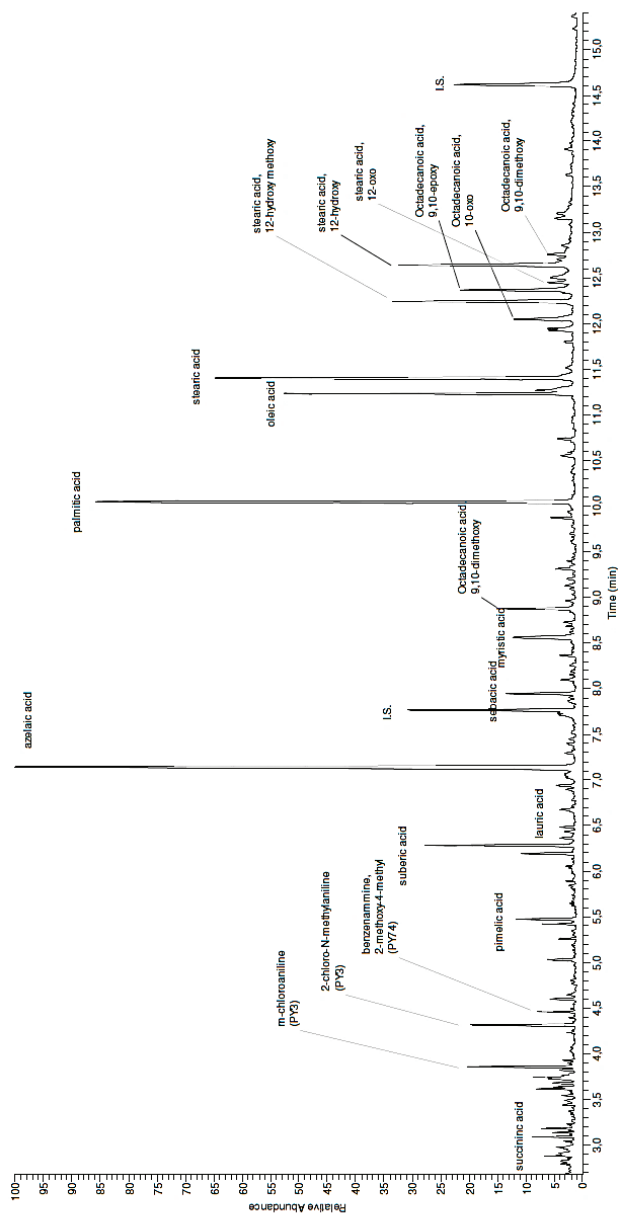


Figure 5. Total ion current pyrogram of Winton yellow oil (OY) paint after transesterification and Py-GC-MS analysis.

For all the yellow paints, variations in the FTIR absorption bands were also observed in the region between 1600-1000 cm⁻¹ corresponding to the 'finger print' region of yellow azo pigments, possibly due to the oxidation of the organic dyestuff as can be seen also in the Py-GC-MS [2]. This trend was less evident for the vinyl and acrylic paints probably due to the greater stability of the polymer binders compared to the oil when exposed to a strong oxidizing agent.

The ozone treatment does not seem to have any effect on the inorganic green and white pigments.

3.2.2 Thermal ageing (T)

Thermal treatment (100°C for 24 hours) clearly affects the visual appearance of the paint films, in particular that of the oil paints. Partial melting of the films and separation of the binders from the paint bulk was in fact observed for all the oil paints.

Acrylic and vinyl films are less affected by the thermal treatment compared with untreated samples.

Table 3 reports the mass variation of the treated paint films after thermal treatment. All samples exhibited a common mass loss associated with the evaporation of volatile products and water.

The mass variations were generally higher for the yellow paints, since organic dyestuff is more sensitive to heat treatment than titanium and chromium oxide based paints [33, 34].

Of all the analyzed paints, acrylic emulsions clearly present the highest variation in mass up to -7.6 % due to their higher water content.

Table 3. Mass variations (%) of paint films after thermal ageing at 100°C for 24 hours and after treatment with relative humidity at 83% for 7 days.

Samples	Mass variations (%)	
	After T ageing	After RH ageing
OG	-2.15	+0.25
OW	-1.73	+0.56
OY	-7.50	+1.34
AG	-3.86	+3.64
AW	-3.01	+3.01
AY	-7.62	+7.21
VG	-2.08	+2.22
VW	-2.92	+2.25
VY	-3.53	+2.91

Figure 6 illustrates the comparison of the FTIR spectra obtained before and after thermal treatment for the different white paint formulations (OW, AW, VW), here reported as a representative example.

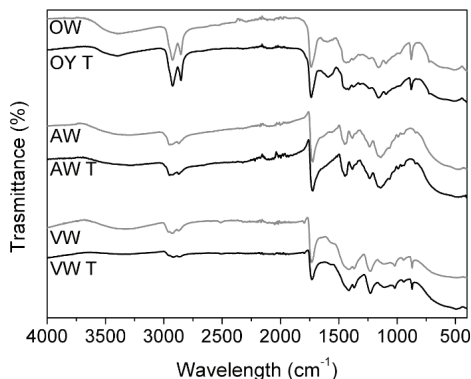


Figure 6. ATR-FTIR spectra of Winton (OW), Liquitex (AW) and Flashe (VW) white paints before and after T treatment

Thermal ageing seems to have a greater effect in the case of vinyl and oil paints even though evident changes can also be observed in acrylic paints. The Flashe paint (VW) exhibits a decrease in the intensity of the binder absorption peaks (CH stretching at around 2900 cm^{-1} , C=O stretching at 1730 cm^{-1} , 1225 cm^{-1}).

In addition to the already observed variations in the binder peaks [31], the formation of metal carboxylates was observed in the oil paints, shown by the typical absorption peak at around 1590 cm^{-1} . As evidenced by XRF analysis, ZnO is present together with TiO_2 in the composition of the Winton white paint (OW). The formation of zinc carboxylates in modern and contemporary oil paints seems to stem from a common process of degradation as previously stated, especially when metal soaps and extra fatty acid sources are added as dispersing agents [35].

3.2.3 Humidity treatment

Changes in the visual appearance of the paint films were recorded in particular for acrylic and vinyl formulations after exposure for 7 days in sealed saturated salt chambers at 83% RH. Acrylic films visually increased their glossiness while vinyl films increased their matte appearance.

All the paints changed in weight as a consequence of the humidity treatment (see Table 3). In general, these changes were more marked for the acrylic and vinyl films as they are more sensitive to humidity than oils [18, 23, 25]. As expected, at 83% RH acrylic films show the highest mass increase up to 7.2 % (Liquitex yellow paint, AY) compared to the untreated ones.

Any relevant chemical variations occurred after humidity treatments for acrylic and vinyl paints. However, as already seen for the thermal treatments, the high level of humidity seems to promote the formation of metal carboxylates for all analysed oil formulations [19, 28].

3.2.4 Total colour changes

Figure 7 shows the overall colour changes of the paint films, calculated by comparing the colorimetric parameters before and after ageing treatment and expressed as ΔE .

Chromatic variations are clearly visible in the case of the Winton white and yellow oil paints which were respectively yellowed and more saturated due to the red component (a^*).

Minor chromatic variations were detected for ozone treatments. On the other hand, when the paints were subjected to T and RH treatments, the high ΔE values recorded were significant, in particular for the Winton white (OW) and yellow (OY) paints.

All the white paints show an increase of the yellow coordinate ($b^*>0$) while the a^* coordinate becomes higher corresponding to a decrease of the green component in the paint colour. The Winton white paint films (OW) present the most significant variations for all the chromatic coordinates: L^* , a^* e b^* . Finally, all the yellow paint films show a similar trend with a decrease of the yellow coordinate ($b^*>0$) and more positive a^* values corresponding to a shift towards red.

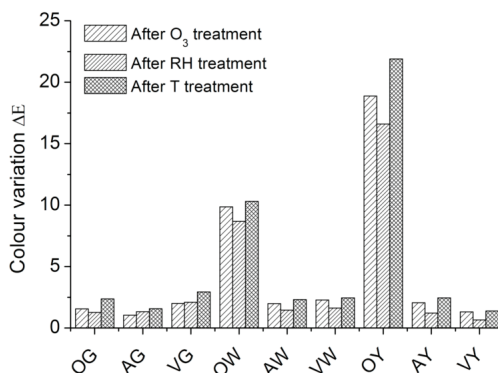


Figure 7. total colour changes (ΔE) of the paint films after ageing treatments

4. Conclusions and future perspectives

This preliminary study provides important information on the composition and behaviour of some commercially available paints, among those most frequently used by young Venetian artists and students from the Academy of Fine Arts: Winton oil paints (Winsor & Newton, UK), Heavy Body acrylic paints (Liquitex, USA) and Flashe vinyl paints (Lefranc & Bourgeois, France).

As expected, the commercial paints investigated show quite complex formulations, where- in addition to the binder and pigments declared in the producers' technical datasheets- several other products were detected:

- Liquitex acrylic paints contain n-butyl acrylate and methyl-methacrylate (n-BA/MMA); Flashe vinyl paints are emulsions of poly-vinyl acetate/vinyl versatate (PVA/VeoVA); Winton oil paints contain linseed oil, but in the case of the white paint (OW) the binding medium is composed of a mixture of linseed oil and safflower oil, the latter being a semi-drying oil;
- additives such as castor wax in the oil paints, dibutylthiocarbamate as a stabilizer in the acrylic emulsions and diisooctyl phthalate as a plasticiser in the vinyl dispersions;
- calcium carbonate was found in the Winton and Liquitex paints as an extender.

The paints were subjected to different accelerated ageing treatments. The results indicate different behaviours in relation both to the type of binder and pigments present in the different formulations. The study has moreover underlined how not only the binding media but the pigments too, are important factors for evaluating the drying behaviour, stability and interactions with respect to the studied range of T, RH and O₃ level.

The results obtained from studying the paint films showed that ozone plays an important role in the stability of oil paints, in particular those containing the yellow azo-pigment (OY); on the other hand, acryl and vinyl paints show minimum variations when subjected to ozone treatment. Temperature, as expected, significantly affected all the commercial paints resulting in the formation of degradation products and visible alterations in the appearance of the paints' aspects. On the other hand, humidity clearly affected acrylic and vinyl paints, commercially found as water emulsions, as was evident in particular in the mass variations.

The influence of the ageing treatments also resulted in clear changes in the paint colorimetric coordinates, in particular for the white and yellow oil paints.

The results of this study can contribute to promoting the development of preventive plans and monitoring campaigns for the conservation of contemporary paintings, paying particular attention to environmental parameters that might influence the stability of the different commercial colours in relation to their chemical composition (binding media, pigments, additives).

Acknowledgements

The authors express their thanks to Dr. Henk van Keulen of the Cultural Heritage Agency of The Netherlands (RCE) for assisting in the Py-GC-MS data interpretations, Dr. Laura Falchi of Ca' Foscari University for her patient help in reviewing the final aspect for the graphs.

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