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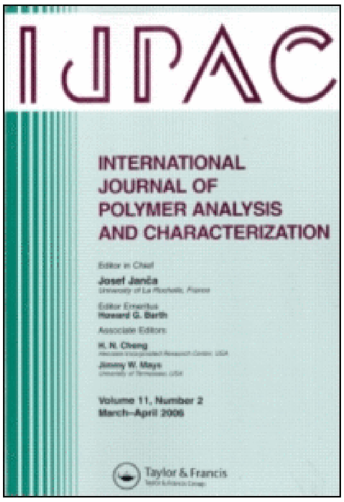

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Characterization of Artists' Acrylic Emulsion Paints

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Characterization of Artists' Acrylic Emulsion Paints

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Commercial waterborne acrylic artists' paints have been characterized with pyrolysis – GC – MS, NMR, size exclusion chromatography and FTIR, and thermogravimetry, for establishing chemical composition, solubility behavior, presence of fillers and additives. In all the pigmented formulations, and in one pure medium, the polymeric base has been invariably found to be formed by different amounts of an ethyl acrylate – methyl methacrylate copolymer. A second acrylic medium revealed the presence of n-*butyl acrylate as a third monomer. Pigmented paints were always more difficult to dissolve than pure media, and the occurrence of insoluble material could be demonstrated with titanium white paints. Inorganic components and other additives present in the paint formulations are expected to have some influence on the chemical and molecular evolution of the paints with aging.*

Keywords: Waterborne acrylic paints; Structural and compositional characterization; Solubility; Additives

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Acrylic polymers are present in many formulations of paints, coatings, and adhesives. Their wide and varied use is due to a favorable combination of appropriate chemical and optical properties, which give rise to durable and high-performance materials that can be manufactured economically. The polymers used for these products are mostly utilized as aqueous dispersions, which are generally obtained from emulsion polymerizations. One of the principal advantages of aqueous polymer dispersions over organic solutions of analogous polymers is that their viscosities are naturally low, even with formulations of high solid content, and therefore their application tends to be more straightforward. Furthermore, they do not suffer from the significant problems of flammability and toxicity brought by the presence of organic solvents. As a result of these properties, waterborne acrylic paints (often referred to as acrylic emulsions) have been developed and widely used as artists' media for paintings[1] and for the conservation of art objects. When an aqueous dispersion is applied to a given surface, the polymer particles come into contact as water evaporates and subsequently fuse together to form a solid and continuous film[2]. The quality of the resulting film is largely controlled by characteristics of the polymer itself, i.e., chemical structure and molecular weight, but also depends heavily on the presence of numerous additives in the systems, such as surfactants, protective colloids, stabilizers, and dispersed pigments.

Many different brands of artists' water dispersed acrylic paints are commercially available, and most of them are based on copolymers of ethyl acrylate (EA) with methyl methacrylate (MMA), although in recent years the EA content has been partly or wholly replaced by *n*-butyl methacrylate (*n*BA)[3,4]. Representative types of acrylic dispersions used in conservation or as painting materials have been investigated from the point of view of film properties and of their aging performance[5–7]. In particular, it has been proposed that room temperature film stabilization in an unpigmented formulation takes an appreciable amount of time (monitored through its mechanical properties)[6], whereas optical changes develop very quickly after application due to phase separation and crystallization of the surfactants in the system[7]. Natural and thermal aging were found to decrease the polymer solubility, and exposure of the aged films to near-UV light irradiation produced scissions in the polymer and a subsequent gain in solubility[6]. Such behaviors differ from the stability characteristics that have been observed for films of similar acrylic copolymers but applied from solution in organic solvents[8,9].

In order to investigate the mechanisms by which acrylic dispersion paint films might undergo chemical and molecular changes under different aging conditions, it is necessary to have detailed composition characterization of the product, with knowledge of all possible features regarding the acrylic component, and also the additives in the system. Consequently we have started an investigation aimed to correlate the structure and composition of acrylic waterborne paints with their aging characteristics, under both natural indoor and accelerated laboratory conditions. In this article we present the results obtained with a combination of techniques regarding the characterization of two series of acrylic commercial artistic paints.

EXPERIMENTAL

Samples of artists' acrylic emulsion paints from two different producers, Lukas (Lukascryl acrylic, Germany) and Royal Talens (Rembrandt acrylic colours, Netherlands), both obtained in 1993, were investigated. Eight different colored paints and one unpigmented medium for each brand were tested (Table I).

Structural characterization of the acrylic polymers was performed with pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). From analysis of the fragmentation patterns obtained, the monomeric units in the paints could be determined. In some cases it was also possible to identify the organic pigment of the paint. All the samples were found to contain acrylic copolymers, and their chemical compositions were determined by nuclear magnetic resonance (NMR). The molecular weight distributions of the polymers were measured by size exclusion chromatography (SEC), and SEC coupled with Fourier transform infrared (FTIR) spectroscopy enabled the identification of the surfactant

TABLE I List of the analyzed paints and media

	Lukas		Royal Talens
1	Acrylic medium brilliant	10	Acrylmedium glossy
2	Lukascryl—Titanium white	11	Rembrandt—Titanium white
3	Lukascryl—Helio genuine yellow lemon	12	Rembrandt—Azo yellow medium
4	Lukascryl—Yellow ochre light	13	Rembrandt—Yellow ochre
5	Lukascryl—Cadmium red light	14	Rembrandt—Cadmium red medium
6	Lukascryl—Vermilion red light	15	Rembrandt—Naphthol red medium
7	Lukascryl—Cobalt blue	16	Rembrandt—Cobalt blue
8	Lukascryl—Helio genuine blue	17	Rembrandt—Phthalo blue
9	Lukascryl—Iron oxide black	18	Rembrandt—Oxide black

employed in the polymerization. Thermogravimetry (TG) was used to determine the amount of organic component in the pigmented paints.

Techniques

Pyrolysis-GC-MS experiments were carried out with an integrated system composed of a CDS Pyroprobe 1000 heated filament pyrolyzer (Analytical Inc., USA), a GC 5890A gas chromatograph (Hewlett Packard, USA), equipped with capillary column HP-5MS cross-linked 5% Ph Me Silicone (30 m × 0.25 mm × 0.25 μm) and a Hewlett Packard GC 5970 mass spectrometer. Pyrolysis was performed at 250°C and 600°C for 10 s. The pyrolyzer interface was set at 250°C and the injector at 280°C. The GC column temperature conditions were as follows: initial temperature 40°C, hold for 2 min, increase at 10°C/min to 280°C, hold for 10 min. Helium gas flow was set at 1 mL/min.

Mass spectra were recorded under electron impact ionization at 70 eV electron energy, in the range from 40–600 m/z. Pyrolysis fragments were identified on the basis of their mass spectra and mass library searches (Wiley 138 and NBS).

Molecular characterization was performed with a modular SEC system composed of a Waters (USA) M-45 pump, a Rheodyne (USA) 7010 injection valve, a differential refractometer ERC 7510 (Erma, Japan), and PL Gel type columns, 10-μm particle diameter. THF solutions were separated from solid impurities by filtration through a 0.45-μm PTFE membrane filter. Calibration between the molecular weights 1,600,000 and 147 was obtained with PMMA narrow distribution standards and *o*-dichlororobenzene. A cubic fit for the calibration curve was used.

FTIR analysis of the polymeric fractions separated by SEC was carried out with an LC-Transform system Series 100 (Lab Connections, Inc., USA). Infrared spectra were collected with a Perkin-Elmer 1710 FTIR instrument (Perkin-Elmer, Inc., USA) with a DTGS detector and a 4 cm^{-1} resolution.

TG measurements were run on a Du Pont Thermal Analyst SDT 2960 (DuPont, USA), under nitrogen and airflow of 90 cm^3/min and a heating rate of 10°C/min up to 800°C. ^{1}H-NMR spectra were measured on a Jeol EX 400 instrument (Jeol USA, Inc., USA), after dissolution of the polymer samples in deuterated chloroform and operating at 100 MHz.

RESULTS AND DISCUSSION

The main products formed in thermal decomposition of acrylic polymers were the respective monomers, together with dimers and trimers in lower amounts. Figure 1 shows the pyrogram obtained from the pyrolysis of Lukas unpigmented medium. The major peaks appearing at low

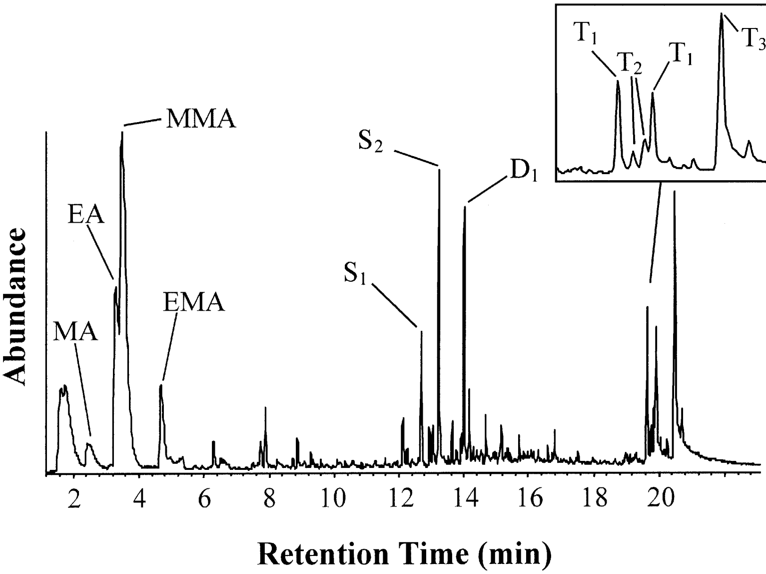

FIGURE 1 Pyrogram of Lukas unpigmented medium by GC-MS. S_1(12.70 min): EA-MMA sesquimer. S_2(13.24 min): EA sesquimer. D_1(14.02 min) EA dimer; T_1(19.63 min): EA-EA-MMA trimer. T_2(19.76 min): MMA-EA-MMA trimer. T_2(19.84 min): EA-MMA-MMA trimer. T_1(19.92 min): EA-MMA-EA trimer. T_3(20.47 min): EA trimer.

retention times were identified as those of ethyl acrylate (EA) and methyl methacrylate (MMA). In the same region, lower intensity peaks of methyl acrylate (MA) and ethyl methacrylate (EMA) were also identified. It is known that these latter compounds may be formed as parent or satellite units in the thermal decomposition of copolymers containing MMA and EA structural units[10]. Assigning the monomeric units that formed the acrylic copolymer was initially based on the observation that the parent peaks were present in much lower concentrations than the EA and MMA monomer peaks. However, in order to exclude the possibility that these parent peaks came from MA and EMA monomeric units that were actually present in low amounts in the acrylic polymer binder, the pyrolysis fragments that were eluted at longer retention times were examined in order to identify the oligomers present. These represent short-chain fragments and would necessarily have been formed by combinations from only those monomers that were present.

In Figure 1, two families of oligomers can be identified, the first with peaks eluting between 12 and 16 min, and the second between 19 and 22 min. The first group of peaks was found to consist of sesquimers

TABLE II Pyrolysis products of Lukas unpigmented medium as determined by Py-GC-MS

Retention time	Identity	M_w
2.43	MA	86
3.28	EA	100
3.48	MMA	100
4.67	EMA	114
12.70	EA-MMA sesquimer (S_1)	188
13.24	EA sesquimer (S_2)	188
14.02	EA dimer (D_1)	200
19.63	EA-EA-MMA trimer (T_1)	300
19.76	MMA-EA-MMA trimer (T_2)	300
19.84	EA-MMA-MMA trimer (T_2)	300
19.92	EA-MMA-EA trimer (T_1)	300
20.47	EA trimer (T_3)	300

and dimers whose principal components are marked in the pyrogram and whose structures and molecular weights, as obtained from analysis of the mass spectra, are reported in Table II. In the second group of peaks, at higher retention volumes, the trimers listed in Table II were identified.

The identification of such oligomeric fragments was more difficult in comparison to the monomeric peaks because their mass spectra did not contain molecular ions. Structural assignments for these, therefore, were made by inspection of the whole mass spectra pattern, with identification of the fragmentation ions produced by the different oligomers. In the sesquimer EA-MMA with molar mass $M = 188$, for example, its mass spectrum (Figure 2) had characteristic lines with m/z 157 and 143, due to the fragments shown, which derive from that particular structure. With the same approach the structure of all the oligomers could be reconstructed. One example from the group of trimers is shown in Figure 3. The trimer EA-EA-MMA (molar mass = 300) may undergo the loss of an ethoxy group (mass 45) or of a methoxy one (mass 31). The ions in the mass spectrum with m/z 255 and 269, respectively, were consistent with this fragmentation pattern and therefore identify this particular trimer.

In the pyrolysis experiments, all the acrylic colored paints tested gave similar results to Figure 1 and Table II, irrespective of manufacturer, and corresponded to a copolymer composed of EA and MMA units. In the unpigmented Lukas medium the molar fraction of MMA was determined by ^{1}H-NMR spectrometry to be 0.39.

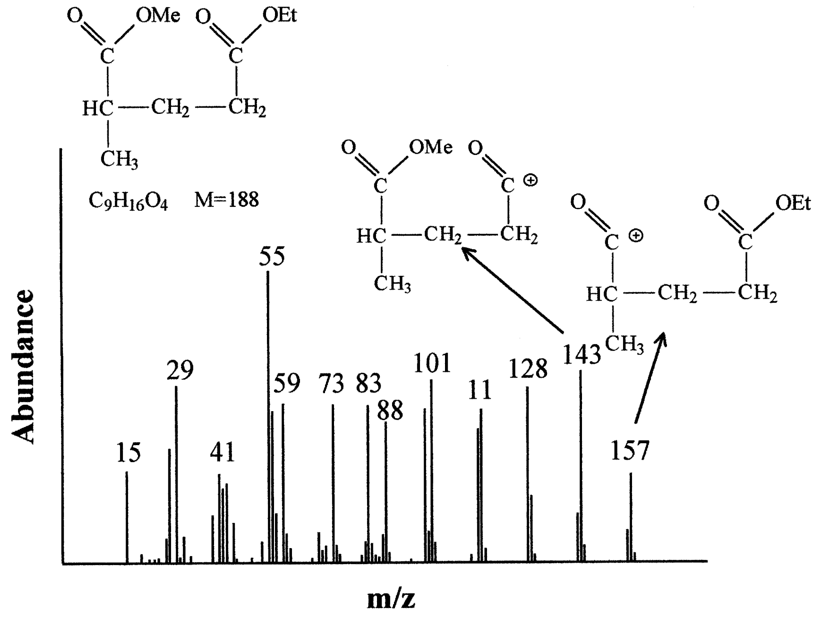

FIGURE 2 Mass spectrum of sesquimer EA-MMA (peak S_1 in Figures 1 and 4).

The structure and composition of the Talens medium turned out to be different. The pyrogram obtained from this sample, seen in Figure 4, also contains a large peak of *n*-butyl acrylate (*n*BA), with the satellite lower peak of *n*-butyl methacrylate (*n*BMA). At the same time it was noticed that in this sample the amount of EA unit appeared to be much lower than in the Lukas medium. The presence of a third monomer leads to a larger number of possible sesquimers and dimers, which were separated in the pyrogram and identified in the same way as previously discussed. The results of the peak analysis for Talens medium are reported in Table III. The molar content of MMA, determined by ^{1}H-NMR, was found to be, in this case, 0.52. The other sample components, EA and *n*BA, account for the remaining 0.48 molar fraction, corroborating the previous observation that the Talens medium contains a lower amount of EA than the Lukas medium.

In the paint pyrograms, the acrylic components were again not affected by the presence of pigments and other additives. In some of the samples, however, organic pigments could be identified from the presence of characteristic pyrolysis products. For example, the presence of yellow azo pigment PY3 is validated by the two peaks of 2-chloro-benzenamine (Figure 5*a*) and 1-chloro-2-isocyanato-benzene (Figure 5*b*), whereas in

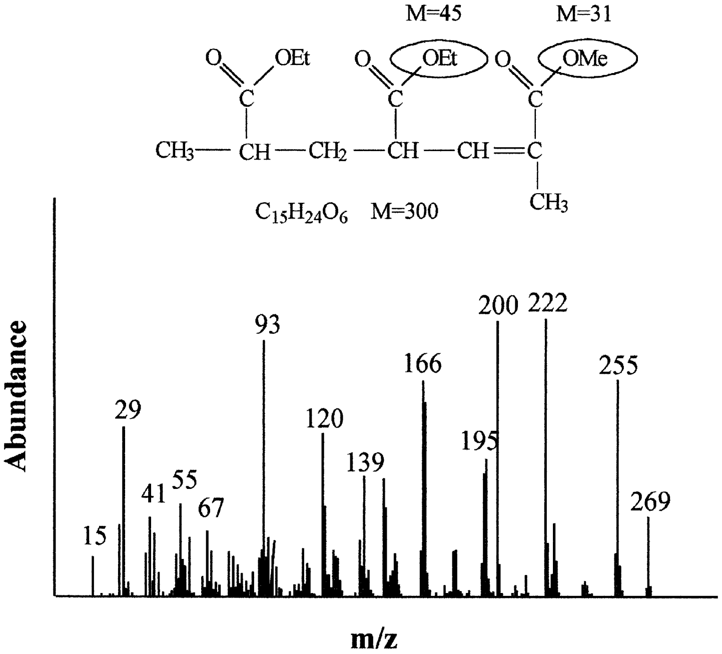

FIGURE 3 Mass spectrum of trimer EA-EA-MMA (peak T_1 in Figures 1 and 4).

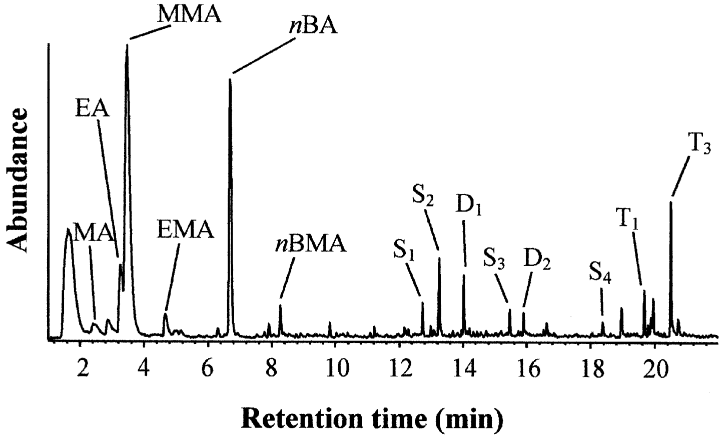

FIGURE 4 Pyrogram of Talens unpigmented medium by GC-MS. S_1(12.73 min): EA-MMA sesquimer. S_2(13.25 min): EA sesquimer. D_1(14.04 min) EA dimer. S_3(15.47 min) *n*BA-MMA sesquimer. D_2(15.89 min): *n*BA-MMA dimer. S_4(18.38 min): *n*BA sesquimer. T_1(19.67 min): EA-EA-MMA trimer. T_3(20.50 min): EA trimer.

TABLE III Pyrolysis products of Talens unpigmented medium as determined by Py-GC-MS

Retention time	Identity	M_w
2.43	MA	86
2.87	butanol	93
3.25	EA	100
3.46	MMA	100
4.66	EMA	114
6.69	*n*BA	128
8.26	*n*BMA	142
12.73	EA-MMA sesquimer (S_1)	188
13.25	EA sesquimer (S_2)	188
14.04	EA dimer (D_1)	200
15.47	*n*BA-MMA sesquimer (S_3)	216
15.89	*n*BA-MMA dimer (D_2)	228
18.38	*n*BA sesquimer (S_4)	244
19.67	EA-EA-MMA trimer (T_1)	300
19.79	MMA-EA-MMA trimer (T_2)	300
19.89	EA-MMA-MMA trimer (T_2)	300
19.95	EA-MMA-EA trimer (T_1)	300
20.50	EA trimer (T_3)	300

the Rembrandt azo yellow sample, the presence of peaks 2-methoxy-benzenamine (Figure 5*c*) and 1-isocyanato-2-methoxy-benzene (Figure 5*d*) indicated the use of another azo pigment, PY74[11]. In addition, many pyrograms showed the presence of propylene glycol, frequently used as an antifreezing agent in water dispersions.

The TG curves under nitrogen flow of the two different unpigmented media showed a one-step volatilization process, according to the expected degradation mechanism for acrylic polymers. At a sufficiently high temperature, all the macromolecular chains are converted into volatile compounds, mainly monomers and oligomers, with a small char residue of about 2% in weight. When executed under air, this residue was completely oxidized, achieving a 100% weight loss. However, the TG curves of the paints, obtained under airflow, showed different and often more complex shapes. In the temperature range between 250°C and 500°C, all the organic constituents, including organic pigments as well as the acrylic resin, were lost. In contrast, inorganic pigments and extenders are generally stable up to more than 800°C. One exception was calcium carbonate, a commonly used extender in paint formulations[12], which started to lose weight at ca. 600°C. From the weight loss due to carbon

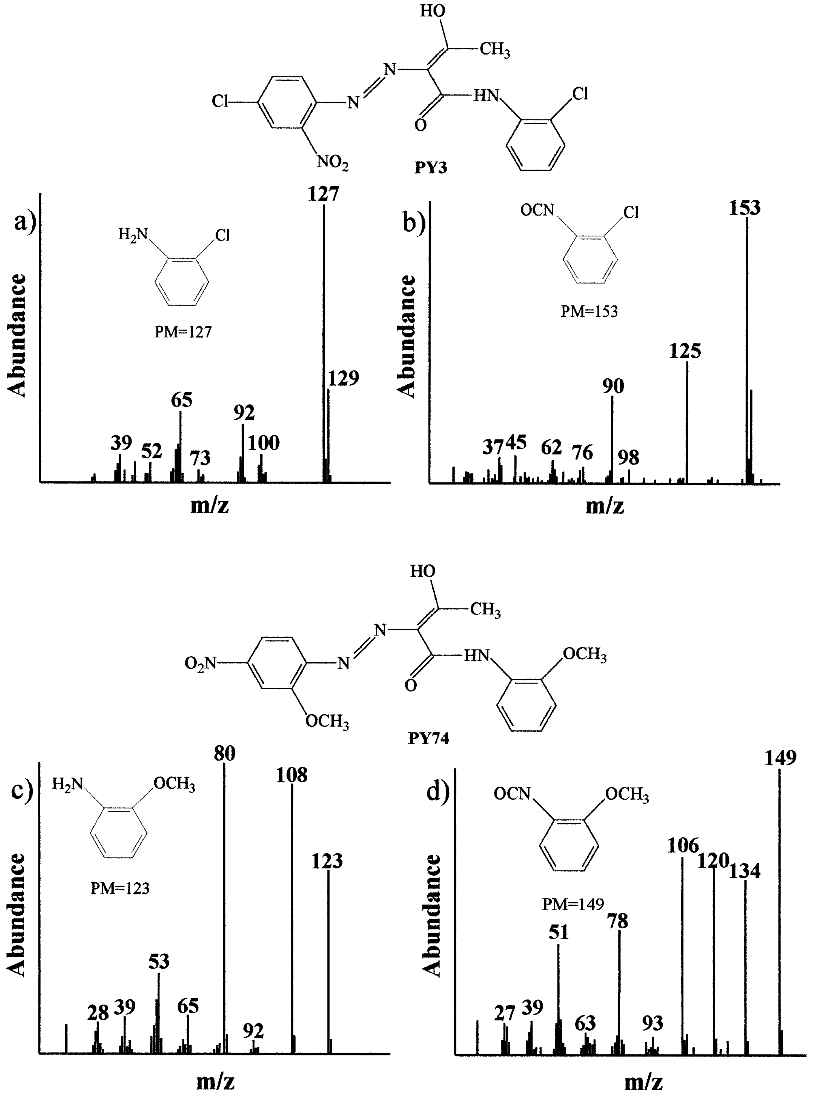

FIGURE 5 Mass spectra of the pyrolysis fragments of pigments PY3 (*a*, *b*) and PY74 (*c*, *d*).

dioxide evolution, it was possible to calculate the amount of carbonate initially present in the sample, the residual calcium oxide, and therefore the weight of the remaining residue due to other extenders and inorganic pigments.

Some inorganic pigments showed particular features at temperatures lower than 800°C. The TG curve in air of Talens cadmium red paint, for example, revealed a weight increase starting at ca. 550°C, attributed to formation of oxidized species (Figure 6). The same analysis carried out under nitrogen showed that in the same temperature range the sample lost weight in two steps, a first one attributed to $CaCO_3$ decomposition, and a second one, whose origin is unknown, at ca. 750°C. Also, Lukas inorganic pigments based on iron oxides (ochre and black) were found to undergo thermally induced modifications. In an inert atmosphere, both ocher and black paint underwent a weight loss at about 740°C. In the presence of oxygen, however, the DTA curves showed a highly exothermic peak, which was attributed to oxidation of the pigments into a more stable form that did not lose weight at 740°C.

Table IV shows the quantities of organic and inorganic components in the paints, as determined from the TG curves. As expected, the organic fraction was observed to be significantly higher for paints containing azo and phthalocyanine pigments compared to those containing inorganic pigments.

The unpigmented acrylic media were completely soluble in THF; SEC chromatograms (Figure 7) reveal two peaks: a broad one representing the molecular weight distribution of the acrylic polymer, and a second one, bimodal in Talens acrylic medium, in the molecular weight region of a

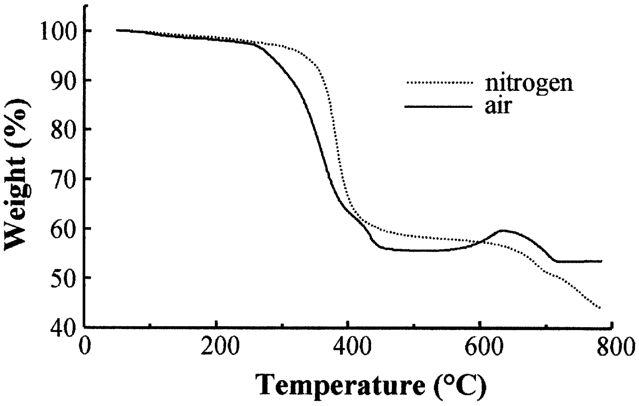

FIGURE 6 TG curves for Talens cadmium red under a stream of nitrogen and air.

TABLE IV Percentage compositions determined from TGA curves

Sample	Weight of the organic component (%)	Weight of the inorganic component (%)	Weight of $CaCO_3$ (%)
Lukas			
Acrylic medium brilliant	100.00	–	–
Titanium white	37.62	62.38	1.45
Helio genuine yellow lemon	42.84	57.16	tr
Yellow ochre light	40.21	59.79	tr
Cadmium red light	39.42	60.58	3.43
Vermilion red light	40.37	59.63	tr
Cobalt blue	38.83	61.17	1.10
Helio genuine blue	52.46	47.54	tr
Iron oxide black	38.45	61.55	1.07
Talens			
Acrylmedium glossy	100.00	–	–
Titanium white	45.23	54.77	8.50
Azo yellow medium	81.60	18.40	17.77
Yellow ochre	61.25	38.75	9.80
Cadmium red medium	44.38	55.61	15.45
Naphthol red medium	76.46	23.54	22.39
Cobalt blue	55.68	44.32	9.48
Phthalo blue	75.62	24.38	19.00
Oxide black	54.31	45.69	12.20

few thousand. The infrared spectra of these low-molecular-weight components were collected after deposition on a rotating germanium disk of the LC-Transform device. The IR spectrum compared closely with a standard spectrum from polyoxyethylene(23)dodecanol (Brij 35), confirming the presence of a poly(ethylene glycol) structure, a widely used class of nonionic surfactant, in the emulsion system (Figure 8). The colored paints were also extracted with THF in order to determine their molecular weight distributions, but it was only possible to extract a fraction of the binder. However, the surfactant peak was present in all of the samples.

The calculated average molecular weights and distributions are summarized in Table V. It may be seen that numerical values of the surfactant peak were very similar (even in the case of Talens acrylic medium where a bimodal distribution is shown). Data relative to the polymer peaks, however, showed differences that are particularly relevant in the case of

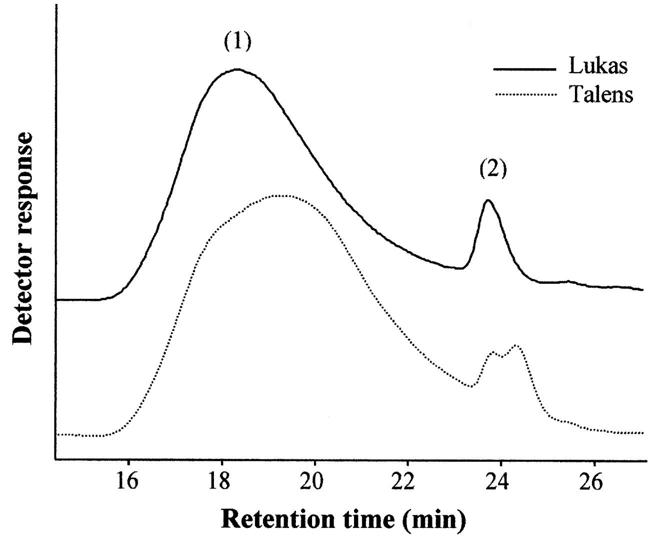

FIGURE 7 SEC curves of Lukas and Talens unpigmented media.

Lukas titanium white and cobalt blue paints. In these two samples the polymer solubility appeared to be quite low, as revealed by the weak detector signals in the chromatograms. The calculated molecular weights were much lower in comparison to other paint samples, suggesting that

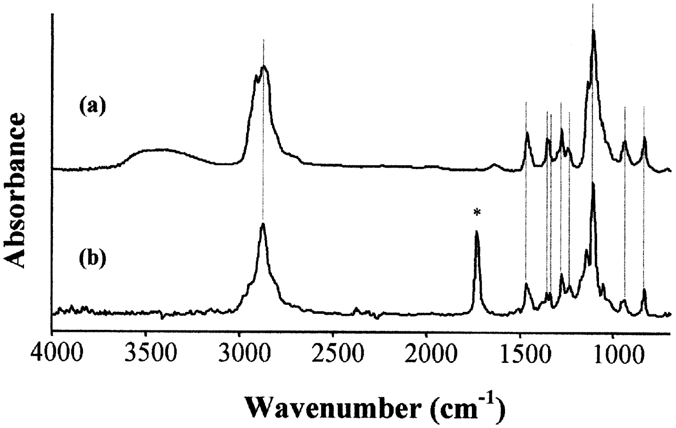

FIGURE 8 FTIR spectra of (*a*) Brij 35, (*b*) surfactant fraction separated from Lukas medium. (*) Impurity due to the acrylic fraction interference.

TABLE V Average molecular weights and molecular weight distributions

	Peak no. 1			Peak no. 2		
Sample	M_n	M_w	D	M_n	M_w	D
Lukas						
Acrylic medium brilliant	$1.17\cdot10^5$	$5.57\cdot10^5$	4.76	$4.99\cdot10^3$	$5.70\cdot10^3$	1.14
Titanium white	$3.80\cdot10^4$	$9.36\cdot10^4$	2.46	$4.57\cdot10^3$	$5.09\cdot10^3$	1.11
Helio genuine yellow lemon	$9.76\cdot10^4$	$5.11\cdot10^5$	5.24	$4.52\cdot10^3$	$4.94\cdot10^3$	1.09
Yellow ochre light	$1.29\cdot10^5$	$5.18\cdot10^5$	4.03	$5.68\cdot10^3$	$6.43\cdot10^3$	1.13
Cadmium red light	$1.02\cdot10^5$	$6.13\cdot10^5$	6.08	$4.92\cdot10^3$	$5.39\cdot10^3$	1.10
Vermilion red light	$1.12\cdot10^5$	$6.17\cdot10^5$	5.47	$5.25\cdot10^3$	$5.76\cdot10^3$	1.10
Cobalt blue	$1.11\cdot10^5$	$6.08\cdot10^5$	5.52	$4.86\cdot10^3$	$5.48\cdot10^3$	1.13
Helio genuine blue	$1.07\cdot10^5$	$5.84\cdot10^5$	5.49	$5.34\cdot10^3$	$5.95\cdot10^3$	1.12
Iron oxide black	$1.02\cdot10^5$	$5.50\cdot10^5$	5.41	$4.88\cdot10^3$	$5.44\cdot10^3$	1.12
Talens						
Acrylmedium glossy	$8.09\cdot10^4$	$4.17\cdot10^5$	5.20	$4.01\cdot10^3$	$4.22\cdot10^3$	1.18
Titanium white	$1.26\cdot10^5$	$7.15\cdot10^5$	5.70	$4.89\cdot10^3$	$5.40\cdot10^3$	1.11
Azo yellow medium	$1.17\cdot10^5$	$6.30\cdot10^5$	5.43	$4.85\cdot10^3$	$5.44\cdot10^3$	1.12
Yellow ochre	$8.17\cdot10^4$	$4.64\cdot10^5$	5.69	$4.56\cdot10^3$	$5.11\cdot10^3$	1.12
Cadmium red medium	$1.14\cdot10^5$	$6.81\cdot10^5$	5.98	$4.47\cdot10^3$	$4.95\cdot10^3$	1.11
Naphthol red medium	$1.24\cdot10^5$	$6.34\cdot10^5$	5.12	$5.19\cdot10^3$	$5.82\cdot10^3$	1.13
Cobalt blue	$4.83\cdot10^4$	$1.56\cdot10^5$	3.21	$4.61\cdot10^3$	$5.06\cdot10^3$	1.10
Phthalo blue	$1.12\cdot10^5$	$6.96\cdot10^5$	6.22	$4.97\cdot10^3$	$5.51\cdot10^3$	1.11
Oxide black	$1.19\cdot10^5$	$6.89\cdot10^5$	5.79	$4.90\cdot10^3$	$5.42\cdot10^3$	1.11

the major part of the acrylic polymer was insoluble. We noticed that all the pigmented acrylic paints were difficult to dissolve completely, even in high polar solvents, and a possible explanation is that during natural polymer aging the inorganic components display catalytic effects in promoting cross-linking reactions. The molecular weights of the polymer peaks in Table V may therefore not be representative of the original polymer molecular weight distributions.

One method for checking the insoluble polymer fraction is to perform TG analysis on the solid residue remaining after the sample treatment with THF, and compare the weight loss of organic components with that measured on the whole paint sample. In Figure 9, the results of such a comparison for the two different titanium white paints are shown. In the TG curves of the Lukas sample, the weight losses of organic component differed by less than 10%, confirming the very low solubility of this sample. The results from Talens titanium white paint were completely different, indicating that the soluble polymer fraction amounted to 73%.

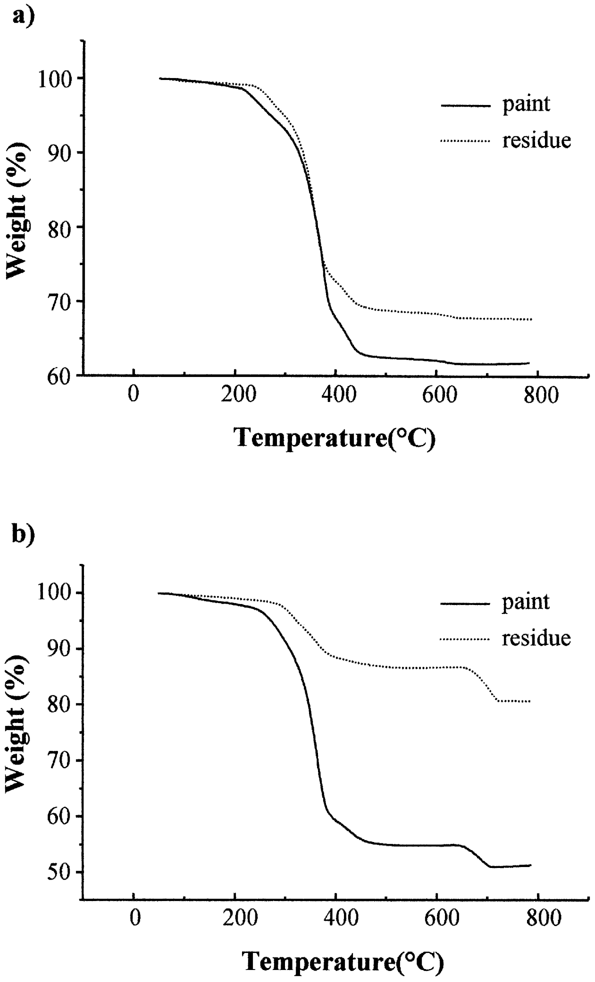

FIGURE 9 TGA curves of the solid residues of titanium white paints after treatment with THF: (*a*) Lukas, (*b*) Talens.

CONCLUSIONS

Artists' waterborne emulsion paints are complex systems, and their characterization needs to distinguish between some structures that are chemically very similar as well as consider the presence and effects of different types of additives. The precise knowledge of copolymer structures and compositions, and of the surfactants and fillers in the emulsions, is a prerequisite for investigating the paint properties and their aging behavior. With a combination of pyrolysis-GC-MS and NMR experiments, the chemical compositions of the acrylic polymer binder could be determined. In the case of the Talens acrylic medium, the higher content of MMA appears to be balanced by the presence of *n*BA in order to display the appropriate film-forming characteristics. It should, however, be taken into account that introduction of *n*BA units induce in the copolymer structure a lower resistance to natural weathering[9,13]. The results obtained on the colored paints indicate that there is a wide formulation variability, even for equivalent colors. The effects and interrelationships between polymer compositions and inorganic components should not be overlooked because they appear to influence the structural-molecular evolution of the paint films.

REFERENCES

[1] Crook, J., and T. J. S. Learner. (2000). The Impact of Modern Paints. London: TGPL.

[2] Feller, R. L. *Bulletin of the American Group-IIC 6*, No. 2 (1966):24–28; 7, No. 1 (1967):18–19; 9, No. 2 (1969):15–17.

[3] Learner, T. J. S. (2000). A review of synthetic binding media in twentieth century paints. *The Conservator* 24:96–103.

[4] Learner, T. J. S. (1995). The analysis of synthetic resins found in twentieth century paint media. In: *Resins Ancient and Modern*, eds. M. M. Wright and J. H. Townsend, Edinburgh: Scottish Society for Conservation and Restoration (SSCR) pp. 76–84.

[5] Howells, R., A. Burnstock, G. Hedley, and S. Hackney. (1984). Polymer dispersions artificially aged. *Adhesives and Consolidants* IIC:36–43.

[6] Whitmore, P. M., and V. G. Colaluca. (1995). The natural and accelerated aging of an acrylic artists' medium. *Studies in Conservation* 40:51–64.

[7] Whitmore, P. M., V. G. Colaluca, and E. Farrell. (1996). A note on the origin of turbidity in films of an artists' acrylic paint medium. *Studies in Conservation* 41: 250–255.

[8] Lazzari, M., and O. Chiantore. (2000). Thermal-ageing of Paraloid acrylic protective polymers. *Polymer* 41:6447–6455.

[9] Chiantore, O., and M. Lazzari. (2001). Photo-oxidative stability of paraloid acrylic protective polymers. *Polymer* 42:17–27.

[10] Wallish, K. L. (1974). Pyrolysis of random and block copolymers of ethyl acrylate and methyl methacrylate. *J. Appl. Polym. Sci.* 18:203–222.

[11] Colour Index. (1971). Bradford, UK: The Society of Dyers and Colourists.

[12] McCleary, R. L. (1975). Calcium carbonate pigments (natural and precipitated types). In: R. R. Myers and J. S. Long eds., *Treatise on Coatings*. New York: Marcel Dekker, Vol. 3, Part 1, pp. 159–259.

[13] Liang, R. H., F. D. Tsay, and A. Gupta. (1982). Photodegradation of poly(*n*-butil acrylate): Photochemical process in polymeric systems. *Macromolecules* 15:974–980.