EVALUATION OF MORPHOLOGICAL CHANGES OF AGED ACRYLIC, KETONE AND HYDROCARBON RESINS USED IN CONTEMPORARY ARTWORKS

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ABSTRACT: *The present work is focused on the study of morphological changes taking place during the ageing of synthetic resins commonly used in contemporary art (paintings, sculpture, ethnographic objects, etc.) by means of optical microscopy, scanning electron microscopy and, as a novelty, atomic force microscopy. The determination of changes in gloss has also been taken into account. For this purpose, the proposed instrumental techniques have been applied on a series of synthetic resin-based varnishes. Preparation procedures have been developed in order to obtain relevant information on the changes in morphology produced during both the ageing process and exposure to a SO_2 saturated atmosphere. Notable changes in the visual appearance of ketone resins, in particular loss of gloss and translucent appearance, are observed which contrasts with the better behaviour exhibited by acrylic resins after ageing, other than a slight yellowing.*

KEYWORDS: AFM, SEM/EDX, acrylic resin, hydrocarbon resin, ketone resin, accelerated ageing, contemporary art

INTRODUCTION

The analysis of works of art is faced with a formidable challenge due to the small amounts of sample available from artefacts. Thus complete characterisation is only possible through the availability of a series of instrumental techniques which provide complementary information. Over the past ten years, instrumental techniques have advanced rapidly both in refinement and the development of new methods. Thus, scanning electron microscopy/x-ray microanalysis (SEM/EDX) has frequently supported archaeometric studies (Schalm et al., 2004; Doménech-Carbó et al., 2001: 571; Roig-Salóm et al. 2003; Burgio et al., 2005; Doménech-Carbó et al., 2006: 123), as have the documentation and interpretation of degradation processes (Doménech-Carbó et al., 2006; Doménech-Carbó et al., 2001: 571), or the assessment of conservation treatments (Doménech-Carbó et al., 2006; Doménech-Carbó and Aura-Castro, 1999). In contrast, a significantly reduced number of works has been published, works which focus on the application of atomic force microscopy (AFM) to the conservation of heritage. Among them, alteration products of historic glass and glaze have been reported to be based on this technique (Schmitz et al., 1997; Schmitz et al., 1995; Hogg et al., 1999) or on the nanoscale characterisation of zoning produced as result of the manufacture of clays in order to obtain Maya blue pigment (Doménech-Carbó et al., 2006: 6027). More recently, a new method of chemical characterisation of pigments has been developed by some of the authors, based on the combination of AFM and nanoparticle voltammetry (Doménech-Carbó et al., in press).

This work focuses on the study of morphological changes taking place during the ageing of synthetic resins commonly used in contemporary art (paintings, sculpture, ethnographic objects, etc.) by means of optical microscopy, atomic force microscopy and scanning electron microscopy. It is interesting to note that this last technique is used here for the first time to characterise morphological changes in pictorial varnishes. The determination of changes in gloss has also been taken into account. The results summarised herein have been obtained in the first series of experiences programmed in the Spanish "I+D+I MEC" project CTQ2005-09339-CO3-01 devoted to the development of new analytical methods for the characterisation of synthetic resins used in contemporary works of art, identification of microbiological alterations and control of biocide treatments. For this purpose, the proposed instrumental techniques have been applied to a series of synthetic resin-based varnishes. Preparation procedures have been developed in order to obtain relevant information on the changes in morphology produced during both the ageing process and exposure to a SO_2 saturated atmosphere.

EXPERIMENTAL

Instrumentation

A Glossimeter Minolta model Multigloss 268 was used to measure changes in gloss of the specimens during ageing.

The surface of the specimens was examined under a Leica stereomicroscope at X2-X40 magnification. Poultice deposited on the surface of the specimens during ageing could be seen at this magnification.

Ageing treatment was also monitored using a cryo-scanning electron microscope Jeol JSM 5410, operating with a Link-Oxford-Isis microanalysis

system and a cryostation CT 1500 C, Oxford Instruments. The analytical conditions were: 10 kV accelerating voltage and $2x10^{-9}$A beam current and 138 K as the working temperature. Sputtering of the sample surfaces with gold or carbon was performed to achieve sample conductivity.

Chemical composition of the particles deposited on the surface of the varnishes was obtained using a Link-Oxford-Isis x-ray microanalysis system. Semi-quantitative microanalysis was carried out using the ZAF method for correcting interelemental effects. The counting time was 100 s for major and minor elements.

To evaluate the surface of the varnishes, a Multimode AFM (Digital Instruments VEECO Methodology Group, USA) with a NanoScope IIIa controller, equipped with a J type scanner (max. scan size of 150x150x6 mm) was used. The topography of samples was studied in the tapping mode. The cantilever (Olympus TappingMode etched silicon probes, Veeco Methodology group) has a spring constant of ~42 N/m and a radius of 5-10 nm to ensure good imaging resolution and nanometer scale indents. Images were obtained using probe excitation frequencies of 300 kHz. All images were captured at a scan rate of 0.5-1 Hz. A set point to a free amplitude ratio (Rsp) of 0.75, corresponding to 25% attenuation of the amplitude of vibration, was used for all images.

Specimen preparation for microscopic examination

In order to perform the AFM, morphological study specimens were prepared by fixing the samples on a steel plate within a thin layer of precoated epoxy at the bottom of the sample. Several images were recorded for all samples at different locations to verify the reproducibility of the observed features.

For the purpose of studying the microscopic texture of the varnish films, top surfaces of the samples were prepared and examined using the Scanning Electron Microscope equipped with a cryostation. After the cryofixation of samples on slush nitrogen, they were sublimated for 10 minutes at 188 K in the scanning electron microscope chamber. Then they were put back into the cryostation to be carbon-coated at 93 K by means of a classic sputtering process. Finally, specimens were placed in the SEM chamber once more for their observation at 62 K.

Artist's materials

The following products, supplied by G.C. Agar-Agar (Vigo, Spain), were used to prepare specimens owing to their wide use in preparing varnishes in conservation studio practices:

a) Acrylic resins Paraloid B72 (copolymer of ethyl methacrylate-methyl acrylate 70/30) and Paraloid B67 (isobtyl methacrylate) manufactured by Rhöm & Haas.
b) Ketone resins: Ketone resin N, Ketone resin MS2-A and Laropal K80 (BASF).
c) Hydrocarbon resin: Regalrez 1094.

Preparation of model varnishes

A series of test specimens were prepared by applying the resin directly on glass slides. In the instances where the resin was supplied as solid product solutions, ranging between 1-5% in acetone, ethanol or xylene were prepared. The freshly prepared model varnishes were spread as a thin layer on glass slides with the help of a thin pencil so that thin films of a thickness less than 10 μm were obtained. Then, the specimens were naturally aged in the dark at room temperature and relative humidity (approximate mean 20ºC 40%) for 1 month prior to testing.

Ageing treatment

Ageing was performed in a SO_2 chamber Dycometal model VCK-300 prepared for test DIN - 50.018 (the Kesternich test). Specimens were maintained in a polluted atmosphere for 15 days. The temperature and relative humidity were maintained at constant values of 40ºC±1ºC and 100%. Concentration of SO_2 during the experiment was maintained at a constant value of 2 l/g.

RESULTS AND DISCUSSION

Visual appearance

Examination of the surface of the specimens was performed after the period of setting and then after ageing. Examination of specimens with both the naked eye and by means of low magnification microscope after setting evidenced that a large number of microparticles were deposited on the surface of the acrylic resins. Part of them were black in colour, suggesting that they were atmospheric carbonaceous particles typical of present-day atmospheric pollution, namely, a result of emissions from domestic heating or industrial plant units, and electricity generating units fuelled by distilled oil or from fuel and coal combustion and automobile traffic.

Drastic changes in the visual appearance of specimens corresponding to ketone resins were observed with the naked eye and by means of low magnification microscope after ageing, as shown in Table 1, where values of gloss shift during ageing are summarised. In particular, loss of gloss and translucent appearance was notably taking place in Laropal and MS2A resins. In contrast, acrylic

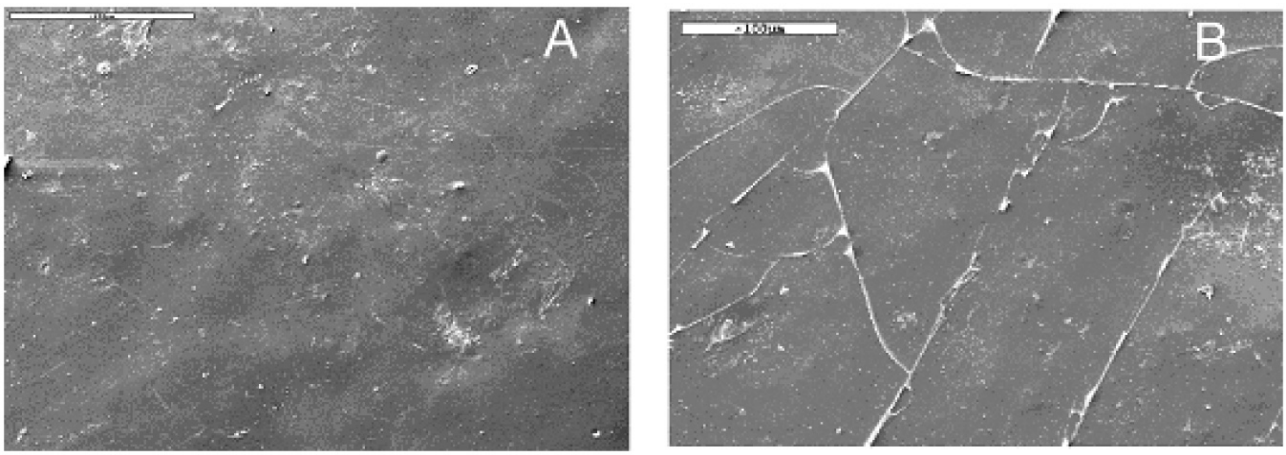

Figure 1. Secondary electron images from Cryo-SEM from: a) Paraloid B72; B)Regalrez

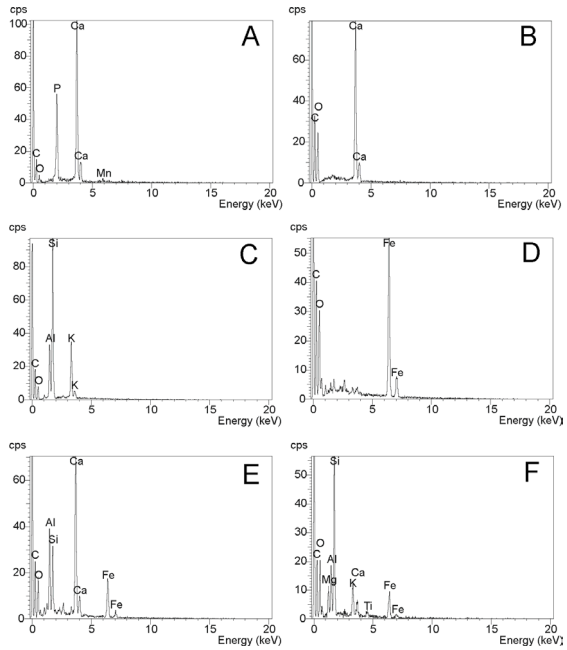

Figure 2. x-ray energy spectra from particles deposed on the surface of Paraloid B72 specimen

Angle of measurement	GLOSS ΔI (20º)	ΔI (60º)	ΔI (85º)
KETON N	-7.8	-14	-8.2
LAROPAL	-21	-13	-16.2
MS 2-A	-19	-24	-11.1
REGALREZ	-12	-4	0
PARALOID B67	-3	-2	-1
PARALOID B72	-4	-3	1

Table 1.

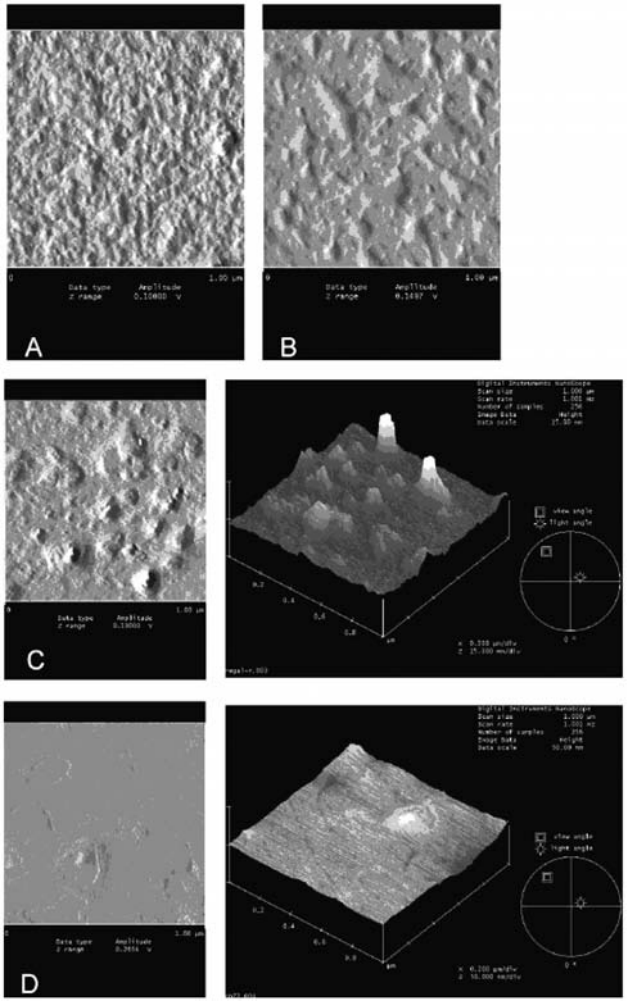

Figure 3. AFM microphotograph of: a) ketone N resin, b) ketone Laropal K80, c) Regalrez, d) Paraloid B72

resins exhibited a more stable behaviour and thus, the translucent appearance was maintained apart from a slight yellowing. Similarly, a minimum loss of gloss was observed in these specimens.

Cryo-SEM/EDX

The surface of the acrylic resin Paraloid B72 and the hydrocarbon resin Regalrez after ageing is shown in Figures 1 a and b, respectively. According to the prior visual examination, Paraloid B72 exhibited a smooth surface where a significant number of microparticles appeared to be deposited, ranging from a few μm to 50 μm. Most of the surface of Regalrez resin specimens appeared to be covered by abundant microfissures resulting in a zonation of the varnish surface with an average zone area ranging from 200 to 400 μm^2. Some particles were seen deposited on the surface of the coating layer.

A chemical characterisation of the particles deposited on the surface of the specimens was carried out by means SEM/EDX. Figure 2 shows the x-ray energy spectra corresponding to the different class of particles identified. As seen in Fig. 2-a, P and Ca-rich particles, associated with calcium phosphate, were recognized together with calcium-rich particles (Fig. 2-b), probably corresponding to calcium carbonate or calcium oxide. Figure 2-c shows the characteristic x-ray emission spectrum of potassium feldspar, whereas Figure 2-d corresponds to the x-ray spectrum of a Fe-rich particle associated with iron or iron oxide. Finally, Figures 2-e and f show the x-ray spectra which are characteristic of clay minerals.

AFM

Figure 3-a shows the topography of the surface of the aged ketone N specimen at a scale of 1 μm. As seen in the image, a pattern of rounded features protruding the surface of the resin on the nanometer scale is seen to range from 0.01 to 0.1 μm. Similarly, figure 3-b, corresponding to the aged Laropal K80 specimen, shows elongated rounded features protruding the surface in the range of 0.1-0.4 μm. These values, in the order of light wavelengths, indicate that the white semiopaque effect observed in these specimens can be due to the light diffusion on the surface pattern made of the rounded features. Fig. 3-c shows both topographical images at 90º and 40º pitch of the Regalrez specimen. This resin exhibits rounded features on a nanoscale range, in the same way as previously described. Additionally, two particles are observed to be deposited on the surface of the coating film. Figure 3-c left allows the determination of the depth of the observed particles, which ranges from 0.3-0.4 μm. These particles are typical atmospheric aerosols. Finally, Figure 3-d shows the topography of the Paraloid B72 specimen at a scale of 1 μm. The surface of this specimen is smoother than that previously described for ketone resins according to the results obtained on optical and scanning electron microscopic examination.

CONCLUSIONS

Notable changes in the visual appearance of ketone resins and hydrocarbon, in particular loss of gloss and translucent appearance, are observed. These contrast with the better behaviour exhibited by acrylic resins after ageing, apart from a slight yellowing.

In contrast, the current study has evidenced that acrylic resins are particularly sensitive to deposition of atmospheric aerosols. Most of the particles deposited on the surface of specimens were typical atmospheric aerosols from soil and only a part of the particles with carbonaceous composition were recognised as typical atmospheric aerosols of an anthropogenic origin. This phenomenon probably took place during the setting period in which specimens were exposed to the environmental air.

AFM examination allows a characterisation of morphological changes at a nanoscale range. The study performed has evidenced that the white semiopaque effect observed on ketone resins after ageing can be due to the slight diffusion on the rounded feature pattern in the order of light wavelengths.

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BIBLIOGRAPHY

Burgio, L., Clark, R., J. H., Sheldon, L., Smith, G.D., (2005): 'Pigment Identification by Spectroscopic Means: Evidence Consistent with the Attribution of the Painting Young Woman Seated at a Virginal to Vermeer', *Analytical Chemistry* **77** 1261-1267.

Doménech Carbó M.T. Aura Castro E., (1999) 'Evaluation of the Phase Inversion Process as an Application Method for Synthetic Polymers in Conservation Works', *Studies in Conservation* **44** 19-28.

Doménech-Carbó, M.T., Casas-Catalán, M.J., Doménech-Carbó, A., Mateo-Castro, R., Gimeno-Adelantado, J.V., Bosch-Reig, F. (2001): 'Analytical study of canvas painting collection from the Basilica de la Virgen de los Desamparados using SEM/EDX, FT-IR, GC and electrochemical techniques', *Fresenius' Journal of Analytical Chemistry* **369** 571-575.

Doménech-Carbó, A., Doménech-Carbó, M.T., Gimeno-Adelantado, J.V., Bosch-Reig, F., Saurí-Peris, M.C., Casas-Catalán, M.J., (2001) 'Electrochemical analysis of the alterations in copper pigments using charge transfer coefficient/peak potential diagrams. Application to microsamples of baroque wall paintings attached to polymer film electrodes', *Fresenius' Journal of Analytical Chemistry* **369** 576-581.

Doménech-Carbó, A.; Doménech-Carbó, M.T.; Más-Barberá, X. 'Identification of lead pigments in nanosamples from ancient paintings and polychromed sculptures using voltammetry of nanoparticles/atomic force microscopy ', *Talanta*, in press.

Doménech-Carbó, M.T. Doménech-Carbó, A. Osete-Cortina, L. Saurí-Peris, M.C. (2006): 'Analytical study of corrosion processes of archaeological glass from the Valencian Region (Spain) and its consolidation treatment', *Microchimica Acta* **154** 123-142.

Doménech-Carbó, A., Doménech-Carbó, M.T., Vázquez de Agredos Pascual, M.L, (2006): 'Dehydroindigo: A New Piece into the Maya Blue Puzzle from the Voltammetry of Microparticles Approach', *Journal of Physical Chemistry* **110** 6027-6039.

Hogg, S.E.T., McPhail, D.S., Oakley, V.L., Rogers P.S. (1999): 'Modern instrumental methods for the study of conservation of vessel glass' in *The Conservation of Glass and Ceramics. Research, Practice and Training*, N.H. Tennent Ed., James & James), London, 42-56.

Roig-Salóm, J.L. Doménech-Carbó, M.T. de la Cruz-Cañizares, J. Bolivar-Galiano, F. Pelufo-Carbonell, M.J. Peraza-Zurita, Y. (2003): 'Study by SEM/EDX and spectrophotometry vis of the stability of resin bound mortars used for casting replicas and filling missing parts of historic stone fountains' *Analytical and Bioanalytical Chemistry* **375** 1176-1181.

Schalm, O., Caluwé, D., Wouters, H., Janssens, K., Verhaeghe, F., Pieters, M. (2004): *Spectrochimica Acta Part B* **59** 1647-1658.

Schmitz, I., Prohaska, T., Friedbacher, G., Schreiner, M., Grasserbauer, M. (1995): 'Investigation of corrosion processes on cleavage edges of potash-lime-silica glasses by atomic force microscopy', *Fresenius Journal of Analytical Chemistry* **353** 666-669.

Schmitz, I., Schreiner, M., Friedbacher, G., Grasserbauer M. (1997): 'Tapping-Mode AFM in Comparison to Cntact-Mode AFM as a Tol for in Situ Investigations of Surface Reactions with Reference to Glass Corrosion', *Analytical Chemistry* **69** 1012-1018.

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Versión española

TÍTULO: ***Evaluación de los cambios morfológicos de resinas acrílicas, cetónicas y de hidrocarburo envejecidas usadas en arte contemporáneo***

RESUMEN: *Este artículo se centra en el estudio de los cambios morfológicos que tiene lugar durante el envejecimiento de resinas sintéticas comúnmente usadas en arte contemporáneo (pinturas, escultura, objetos etnográficos, etc.) por medio de la microscopía óptica, de la microscopía electrónica de barrido y, como novedad, mediante microscopía de fuerza atómica. También se han tenido en cuenta cambios en el brillo. Para este propósito, las técnicas instrumentales propuestas se han aplicado en una serie de muestras de barnices de resinas sintéticas. Se han desarrollado procedimientos de preparación con el propósito de obtener información relevante sobre los cambios en la morfología producidos durante el proceso de envejecimiento y la exposición a una atmósfera saturada de SO_2. Se observan cambios notables en la apariencia visual de las resinas cetónicas, en particular, la pérdida de brillo y el aspecto translúcido, que contrasta con un mejor comportamiento mostrado por las resinas acrílicas después de envejecer, si bien éstas amarillean levemente.*

PALABRAS CLAVES: *El AFM, SEM/EDX, resina acrílica, resina de hidrocarburo, resina cetónica, envejecimiento acelerado, arte contemporáneo*