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Imaging analytical studies of lead soaps aggregating in preprimed canvas used by the Hudson River School painter F.E.Church.

Jaap Boon*, Katrien Keune* and Joyce Zucker**

*Molecular Paintings Research Group, FOM Institute AMOLF, Kruislaan 407, 1098 SJ, Amsterdam, Netherlands.
** Bureau of Historic Sites, Office of Parks, Recreation and Historic Preservation, Peebles Island (New York, USA)

Severe deterioration effects disturb the appearance of many paintings from the late 19^{th} C Hudson River School [1]. One of these problems is the presence of variable translucency of the paint leading to dark patches in the paint, a phenomenon known as ground staining. Other problems are the appearance of surface irregularities due to dynamic processes underneath the paint surface and the formation of blooms and efflorescent crusts. Alterations in paint composition of the ground were studied in a preserved preprimed canvas (OL 1984.NA) dating from the mid 19^{th} century that has been used by F.E.Church as support for his paintings. The purpose of the microscopic spectroscopic studies was to understand the nature of the surface crusts and to image subsurface distributions of organic and inorganic materials using specular reflection microFTIR (FTS-6000 Stingray Digilabs), imaging SIMS (Trift II Phy Electronics) and SEMEDX (FEI XL30 SFEG) [2].

The surface of the paint (Fig. 1A) shows several round protruding masses (diam. ~100 micron) and white efflorescent crusts. Microscopy FTIR shows that the efflorescence mainly consists of lead metal carboxylates [3: J. van der Weerd, PhD thesis, 2002]. Free fatty acids (FA), monoglycerides (MG) and lead soaps of palmitic and stearic acid are observed by imaging SIMS (1B). GCMS studies [3: Van den Berg, PhD thesis, 2001] confirm that most of the fatty acids moieties in the paint layers are no more ester bound (88% hydrolysed). The appearance of some of these compounds at the surface implies that there is insufficient binding capacity for stabilization in ionomeric networks inside the paint. The lump of transparent lead soap (FTIR see [2]; SIMS data resemble 1B) accumulating in the paint layer system (1C-G) is further evidence for the mobility of fatty acids or their soaps. The BSE map (1C) shows this aggregate as a greyish poorly electron reflecting mass in the paint buildup of highly electron reflecting lead white paint (L) at the top with a mixed calciumcarbonate/lead white paint underneath and a calcium carbonate (CaCarb) layer at the bottom. The lead soap mass is not homogeneous: core is less BSE reflective than the rim. Imaging SIMS (after surface is coated with 2 nm gold) demonstrates unique data of monocarboxylic lead soaps (1E) concentrated in the core, while diacids (azeleic acid is featured in 1F) can be detected in the rim of the aggregate. This points to phase separation in the process of formation of crystalline (?) soap structures. There are also high yields of fatty acids (stearic acid ions in 6C) in the paint layer in general.

Efflorescence and lead soap aggregation suggest strongly that there is a surplus of monocarboxylic acid lead soaps in the priming ground. Church himself complained the treatement of the preprimed canvas with lead acetate solutions [1]. We present the hypothesis that Church was painting on a medium rich ground, possibly enriched in monocarboxylic acids by the manufacturers. The lead acetate may have provided a good reactive substrate for the rapid formation of lead soaps separating monocarboxylic lead soaps in an early stage from the other oil paint constituents.

[1]. J.Zucker (1999). JAIC 38, 3-20.
[2]. K,Keune and J.J.Boon (2004).AC 76, 1374-1385
[3]. Down loadable from www.amolf.nl/publications

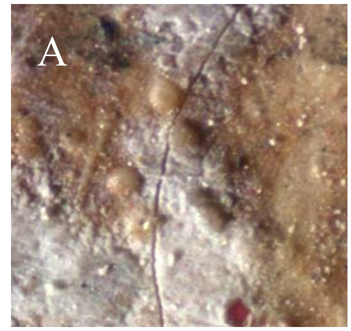
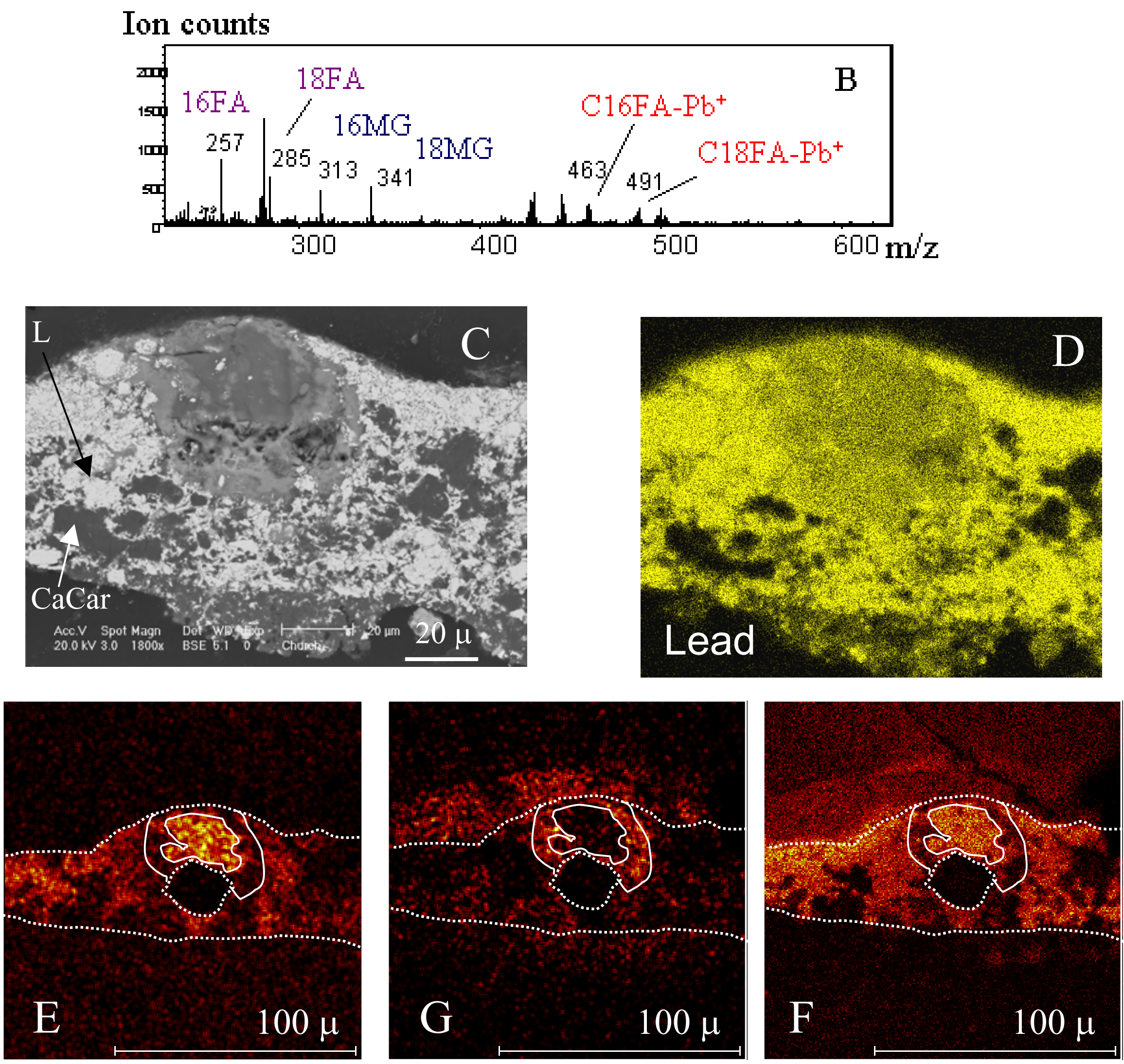


Fig. 1A-G featuring the surface of the preprimed canvas (A), the SIMS spectrum of the efflorescent crust (1B), SEMEDX (1C & D) and imaging SIMS data of a gold coated (2 nm!) cross section with a protruding lead soap mass showing the map of palmitic acid lead soap (+ ions m/z 461-463) (1E), azeleic acid (- ions m/z 187) (1F) and stearic acid (- ions m/z 283) (1G).



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