

Supporting Information for

Oxidation and cross-linking in the curing of air-drying artists' oil paints

Silvia Pizzimenti^a, Luca Bernazzani^a, Maria Rosaria Tinè^a, Valérie Treil^b, Celia Duce^{a*}, Ilaria Bonaduce^{a*}

^a*Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, I-56124, Pisa, Italy*

^b*Département de Chimie, Ecole normale supérieure de Lyon, 15 parvis René Descartes, Lyon, 69342, France*

*co-corresponding authors. Email: celia.duce@unipi.it, ilaria.bonaduce@unipi.it

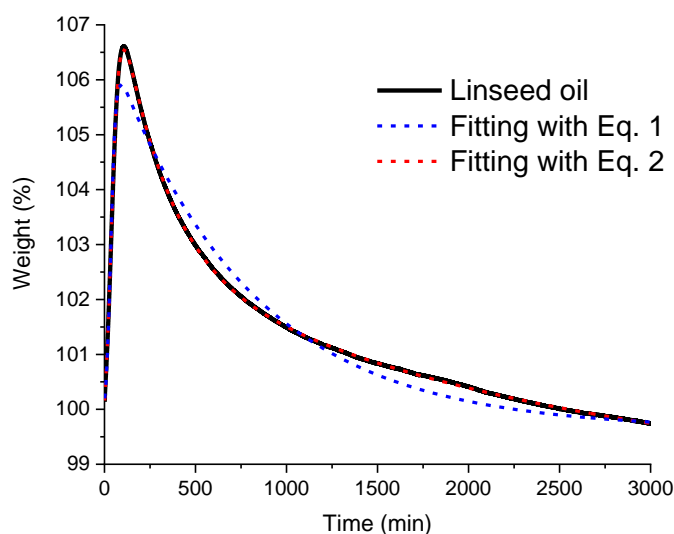


Figure S1. Oxygen uptake profiles of linseed oil, experimental (black line), and theoretical as obtained by Equation 1 (blue line) and Equation 2 (red line)

$$\mathit{mass}\%(\mathit{t}) = \frac{A \cdot e^{-\lambda_1 t}}{1 + e^{-\lambda_0(t-t_0)}} + B \quad (1)$$

$$\mathit{mass}\%(\mathit{t}) = \frac{A \cdot [q \cdot e^{-\lambda_1 t} + (1-q) \cdot e^{-\lambda_2 t}]}{1 + e^{-\lambda_0(t-t_0)}} + B \quad (2)$$

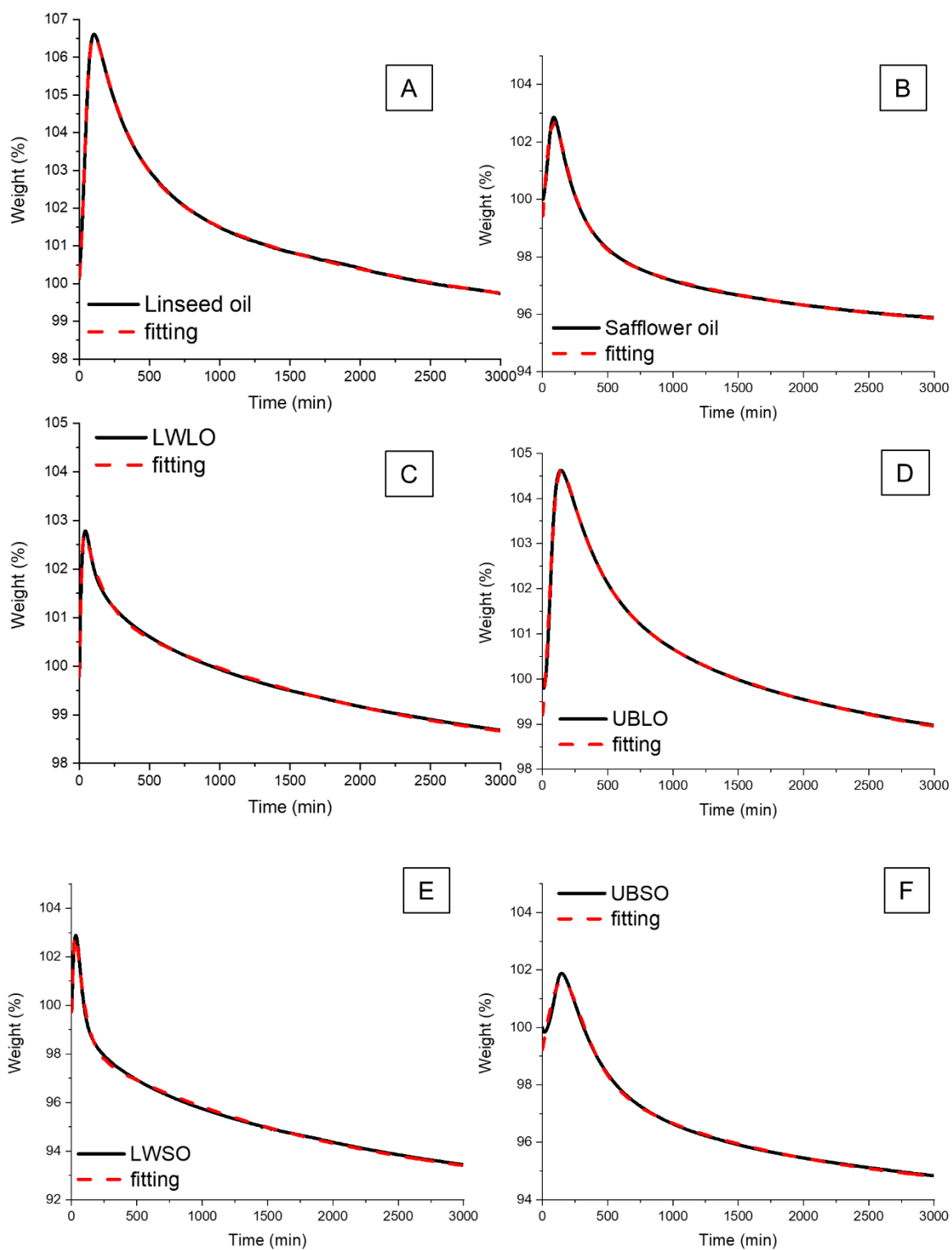


Figure S2. Oxygen uptake profiles of A) linseed oil, B) safflower oil, C) LWLO, D) UBLO, E) LWSO) and F) UBSO paints, experimental (black), and theoretical as obtained by Equation 2 (red) previously reported (Equation 1 in the manuscript).

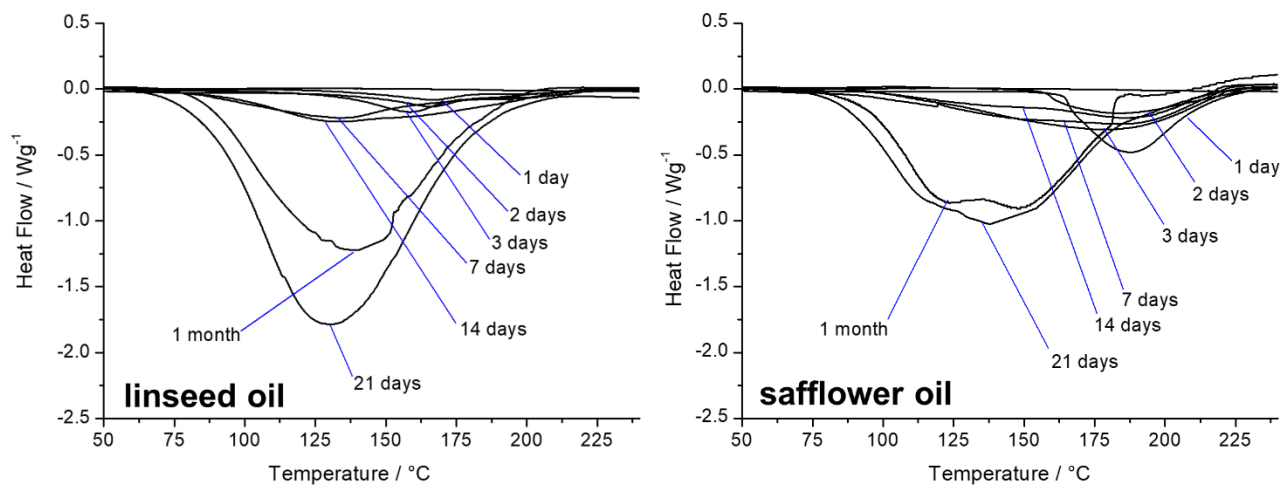


Figure S3. DSC curves of linseed oil and safflower oil recorded during time up to 1 month of natural ageing.

Table S1

T_{onset} , T_{peak} of the normalised DSC curves for linseed oil (LO), LWLO and UBLO.

	LO		LWLO		UBLO	
	T_{onset} (°C)	T_{peak} (°C)	T_{onset} (°C)	T_{peak} (°C)	T_{onset} (°C)	T_{peak} (°C)
1 day	128	166	95	119	-	-
2 days	129	165	90	127	-	-
3 days	124	158	95	116	108	162
7 days	76	135	91	108	92	141
9 days	-	-	91	114	88	140
14 days	77	133	91	111	97	149
21 days	76	132	-	-	-	-
1 month	77	137	-	-	100	161

Table S2

T_{onset} , T_{peak} of the normalised DSC curves for safflower oil (SO), LWSO and UBSO.

	SO		LWSO		UBSO	
	T_{onset} (°C)	T_{peak} (°C)	T_{onset} (°C)	T_{peak} (°C)	T_{onset} (°C)	T_{peak} (°C)
1 day	163	188	99	129	-	-
2 days	157	182	95	127	-	-
3 days	97	177	97	125	115	171
7 days	92	181	87	107	97	138
9 days	85	186	76	98	85	144
14 days	80	137	69	91	97	144
1 month	88	148	-	-	103	154

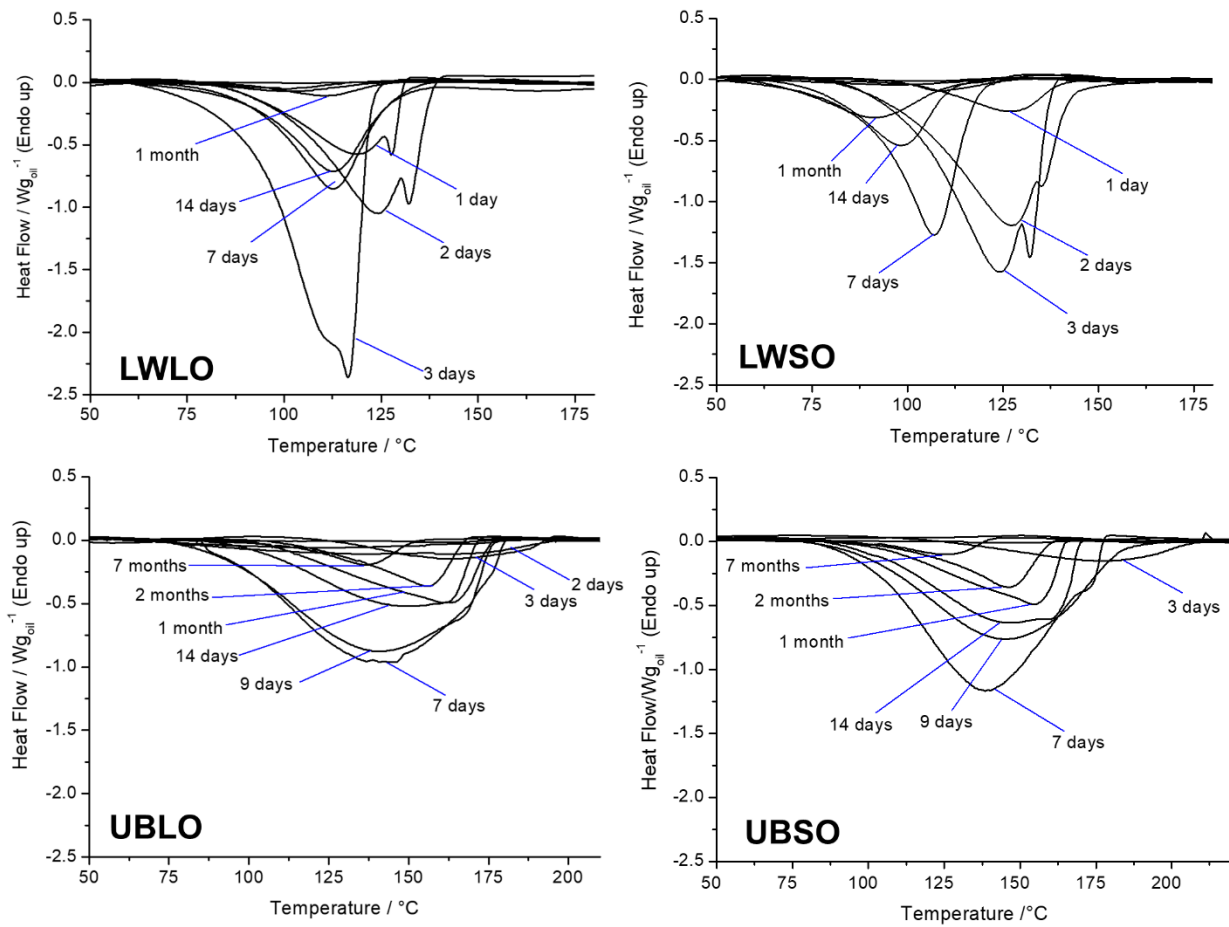


Figure S4. DSC curves peak - normalized to the oil content of the freshly prepared paints - of LWLO, UBLO, LWSO and UBSO paints, recorded during time up to 24 months of natural ageing.

Table S3

List of compounds identified as trimethylsilyl derivatives in the chromatograms obtained by GC-MS and Py-GC-MS of LWLO, UBLO, LWSO and UBSO paints after 7 and 24 months of natural ageing.

N°	Compound	GC-MS	Py-GC-MS	N°	Compound	GC-MS	Py-GC-MS
1	Hexenoic acid		x	23	Heptandioic acid	x	x
2	Hexanoic acid		x	24	8-hydroxydec-9-enoic acid		x
3	2-hydroxypentanoic acid	x		25	8-hydroxyundec-10-enoic acid		x
4	2-hydroxyhexanoic acid	x		26	Octanedioic acid (suberic acid)	x	x
5	Heptenoic acid		x	27	Nonandioic acid (azelaic acid)	x	x
6	Heptanoic acid		x	28	Tetradecanoic acid (myristic acid)	x	x
7	2-hydroxyheptanoic acid	x		29	Decandioic acid (sebacic acid)	x	x
8	Octenoic acid		x	30	2-hydroxynonanedioic acid	x	
9	Octanoic acid		x	31	Hexadecanoic acid (palmitic acid)	x	x
10	2-hydroxyoctanoic acid	x		32	2-hydroxydecanedioic acid	x	
11	3-hydroxyoctanoic acid	x		33	2-hydroxyundecanedioic acid	x	
12	Nonenoic acid		x	34	Cis-octadecenoic acid (oleic acid)	x	x
13	Nonanoic acid		x	35	Trans-9-octadecenoic acid (oleic acid)		x
14	2-hydroxynonanoic acid	x		36	2-hydroxyhexadecanoic acid	x	
15	Decenoic acid		x	37	Octadecanoic acid (stearic acid)	x	x
16	Decanoic acid		x	38	9-12-octadecadienoic acid (linoleic acid)		x
17	2-hydroxydecanoic acid	x		39	9-12-octadecadienoic acid (linoleic acid) isomer		x
18	Hexanedioic acid		x	40	9-12-octadecadienoic acid (linoleic acid) isomer		x
19	Undecenoic acid		x	41	2-hydroxyoctadecanoic acid	x	
20	Undecanoic acid		x	42	9-hydroxyoctadec-12-enoic acid		x
21	Dodecenoic acid		x	43	Eicosanoic acid (arachidic acid)	x	x
22	Dodecanoic acid (lauric acid)	x	x	44	9,10-dihydroxyoctadecanoic acid	x	

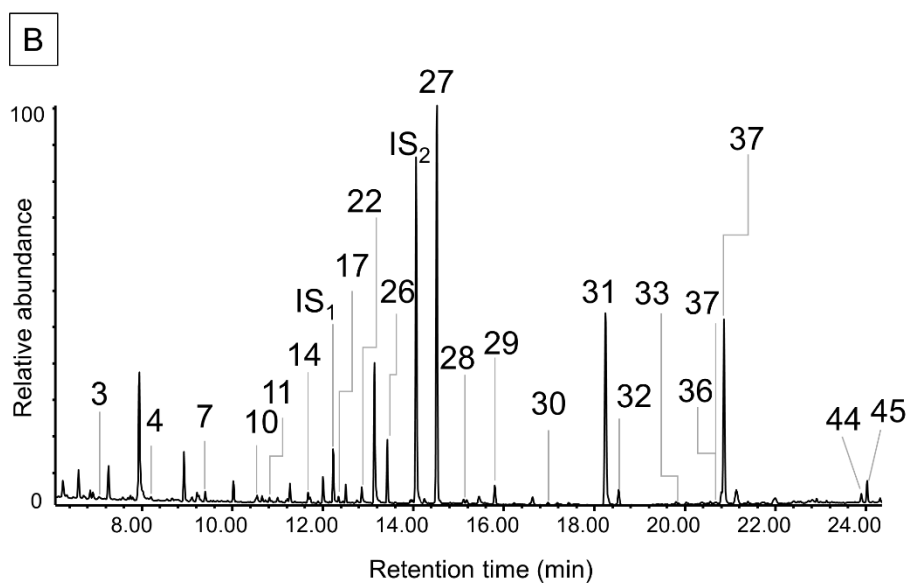
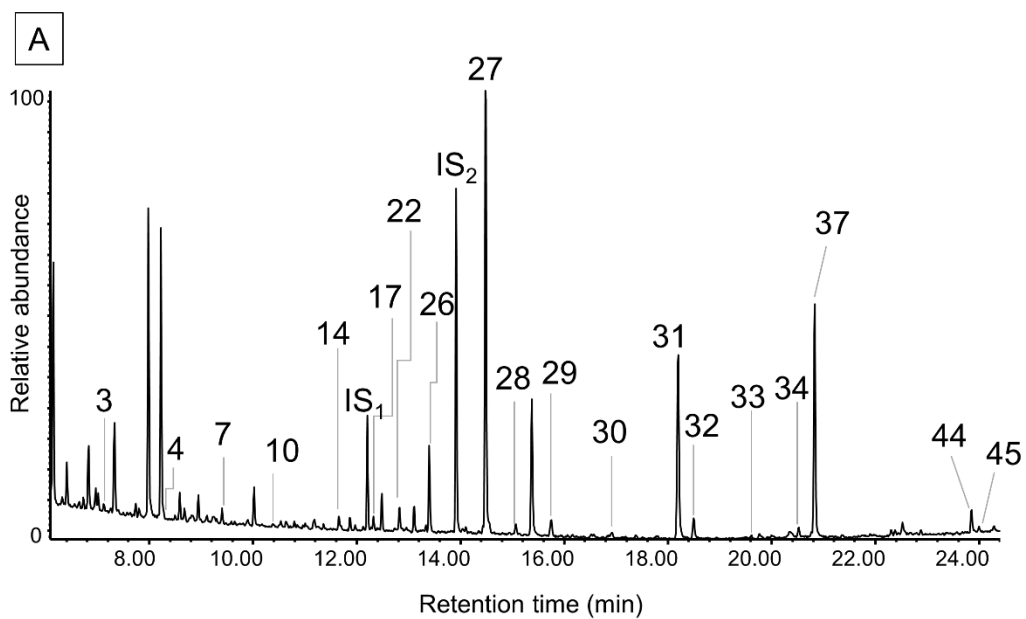


Figure S5. Total ion chromatograms obtained by GC-MS analysis of A) 7 months and B) 24 months films naturally aged LWLO paint. Peaks refer to **Table S3**. IS₁ and IS₂ are the internal standards and referred to hexadecane and tridecanoic acid respectively.

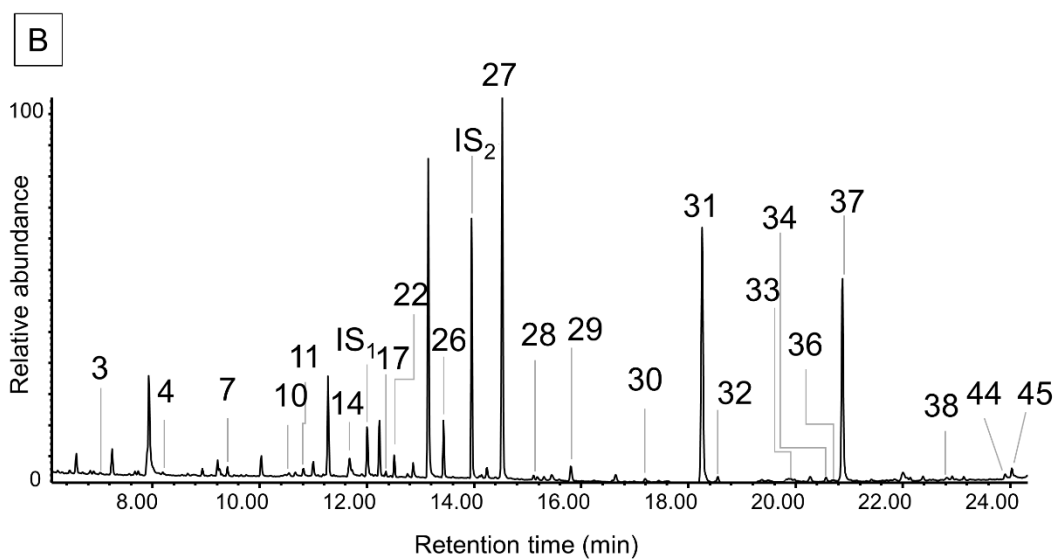
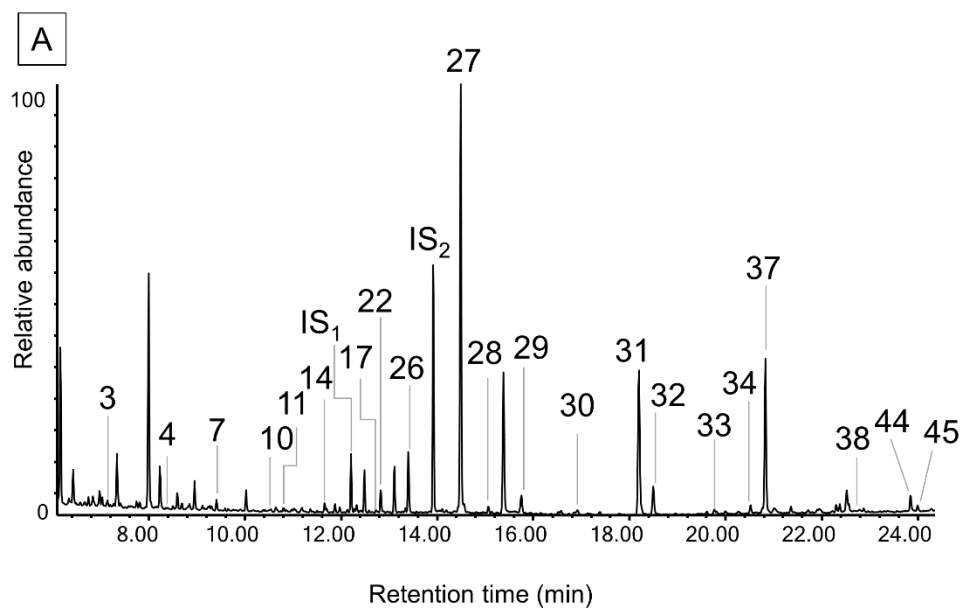


Figure S6. Total ion chromatograms obtained by GC-MS analysis of A) 7 months and B) 24 months naturally aged UBLO paint. Peaks refer to **Table S3**. IS₁ and IS₂ are the internal standards and referred to hexadecane and tridecanoic acid respectively.

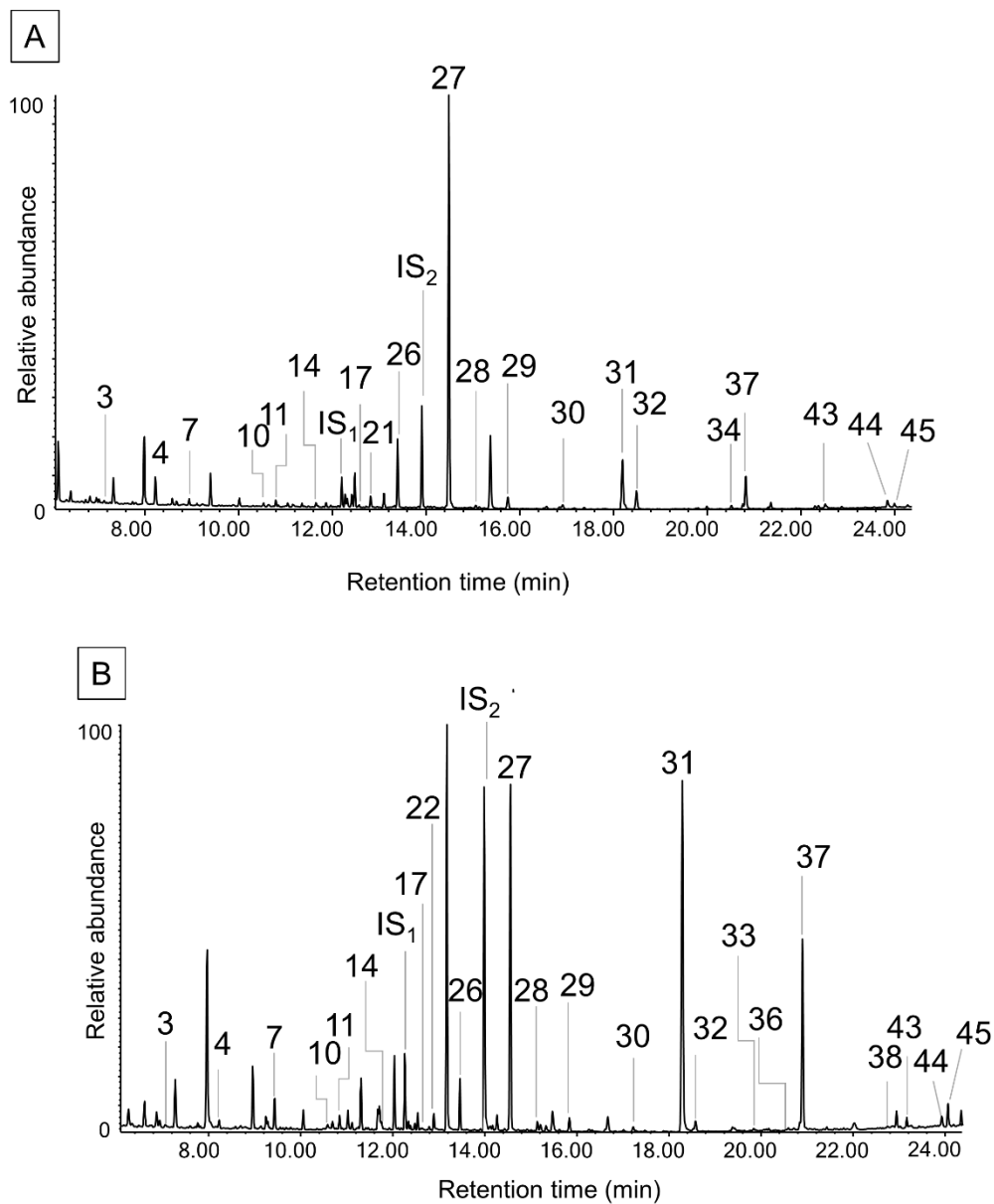


Figure S7. Total ion chromatograms obtained by GC-MS analysis of A) 7 months and B) 24 months naturally aged LWSO paint. Peaks refer to **Table S3**. IS₁ and IS₂ are the internal standards and referred to hexadecane and tridecanoic acid respectively.

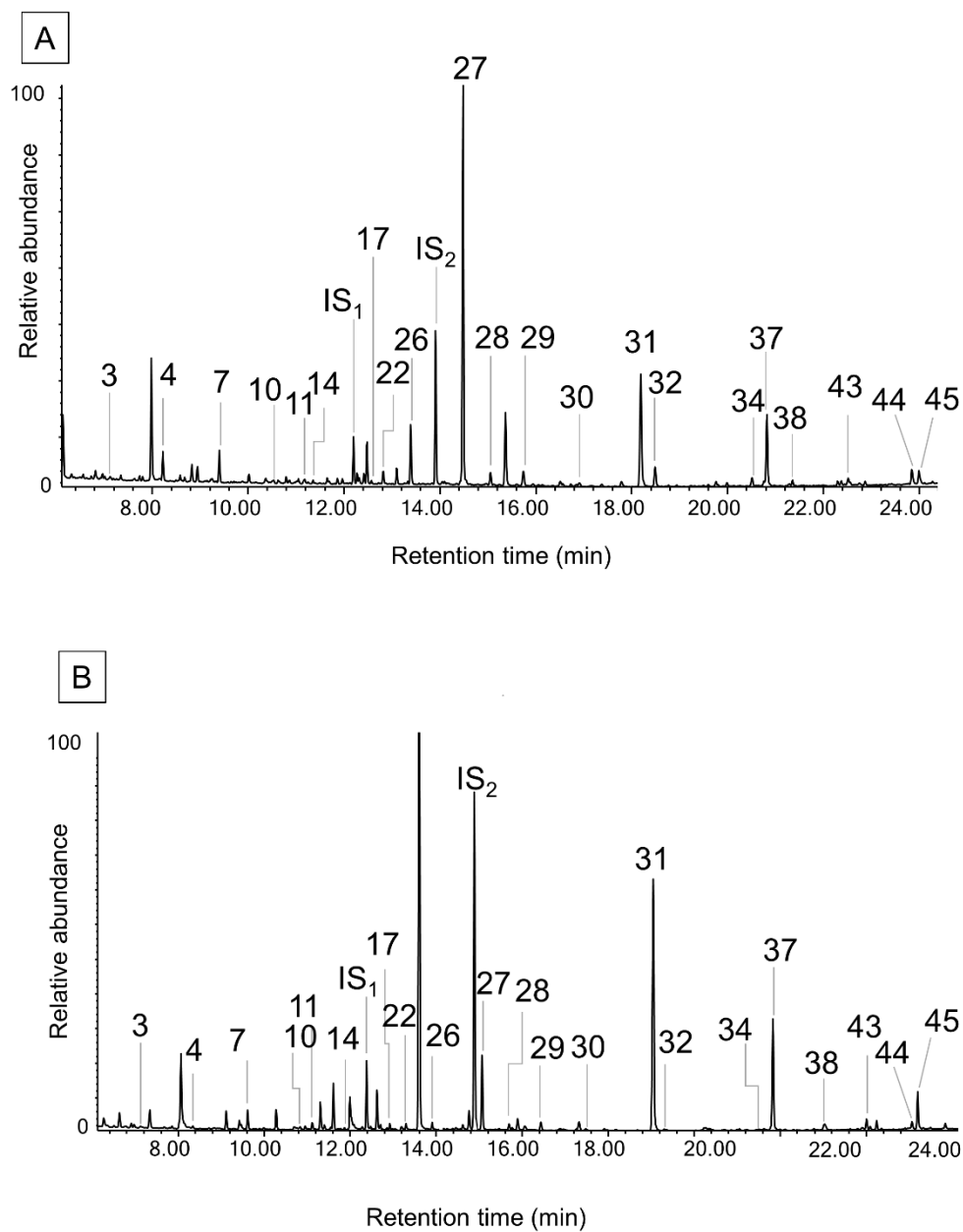


Figure S8. Total ion chromatograms obtained by GC-MS analysis of A) 7 months and B) 24 months naturally aged UBSO paint. Peaks refer to **Table S3**. IS₁ and IS₂ are the internal standards and referred to hexadecane and tridecanoic acid respectively.

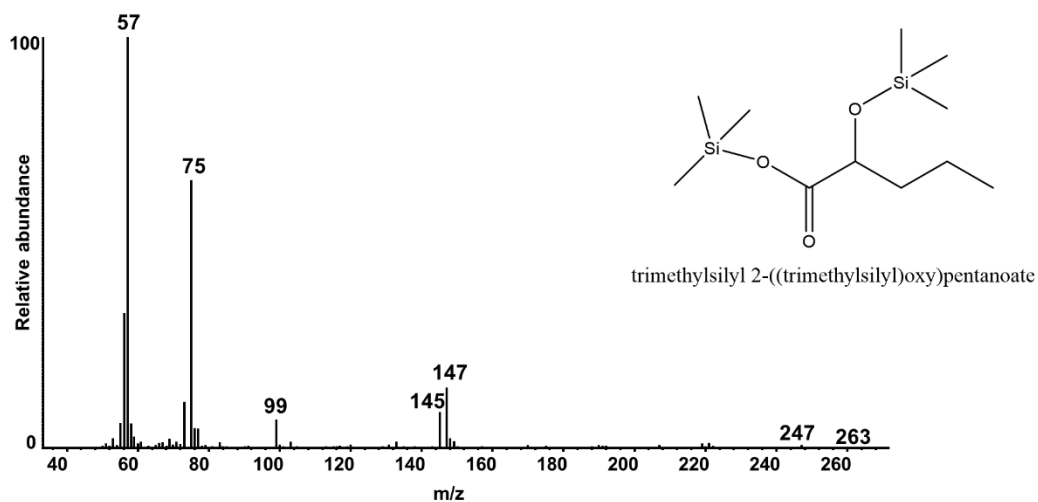


Figure S9. Mass spectrum of trimethylsilyl 2-((trimethylsilyl)oxy)pentanoate obtained with GC-MS.

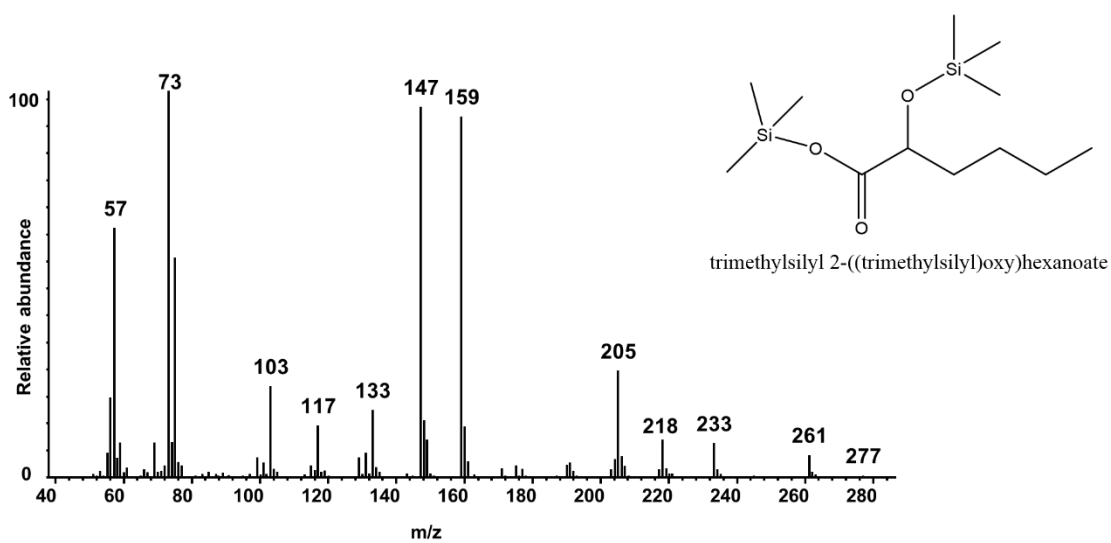


Figure S10. Mass spectrum of trimethylsilyl 2-((trimethylsilyl)oxy)hexanoate obtained with GC-MS.

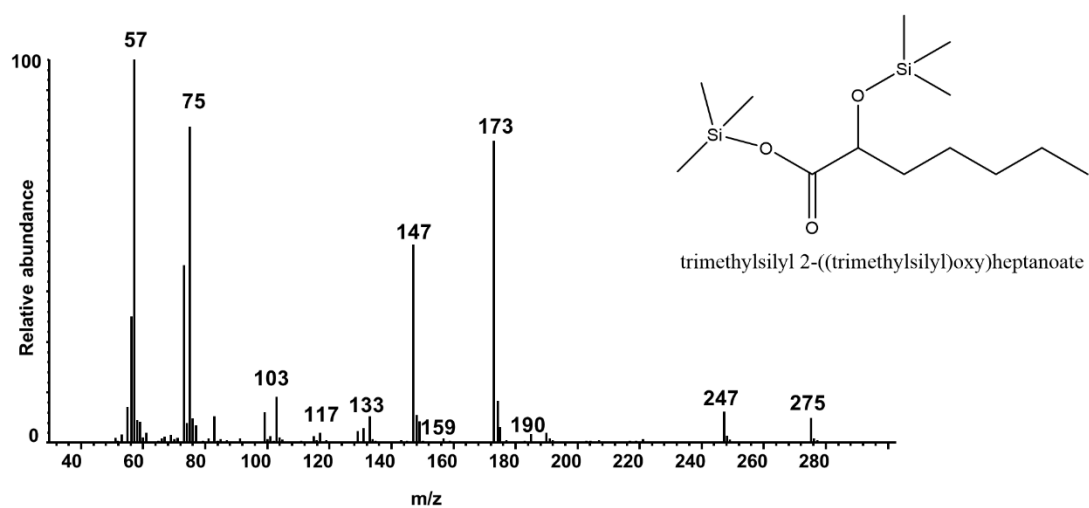


Figure S11. Mass spectrum of trimethylsilyl 2-((trimethylsilyl)oxy)heptanoate obtained with GC-MS.

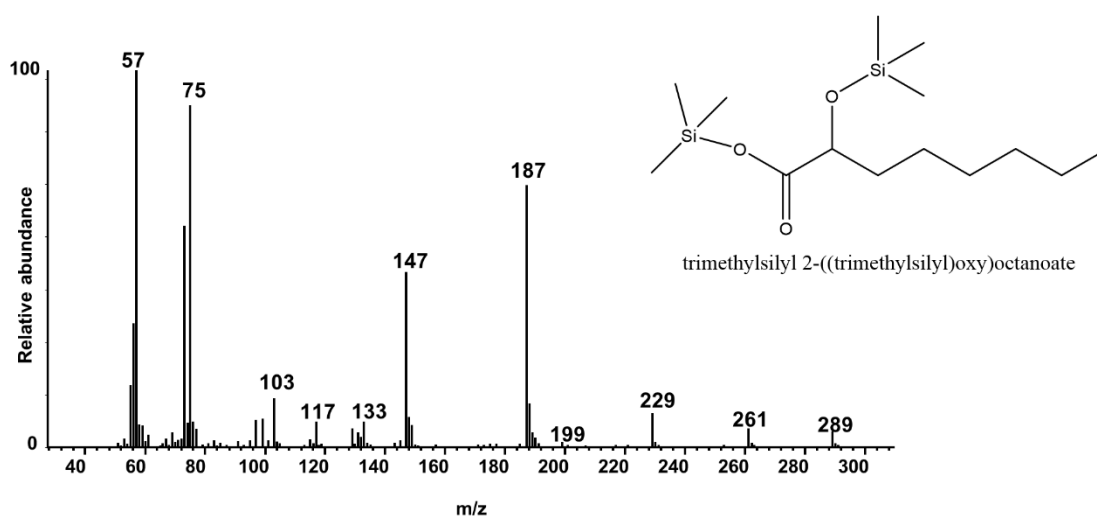


Figure S12. Mass spectrum of trimethylsilyl 2-((trimethylsilyl)oxy)octanoate obtained with GC-MS.

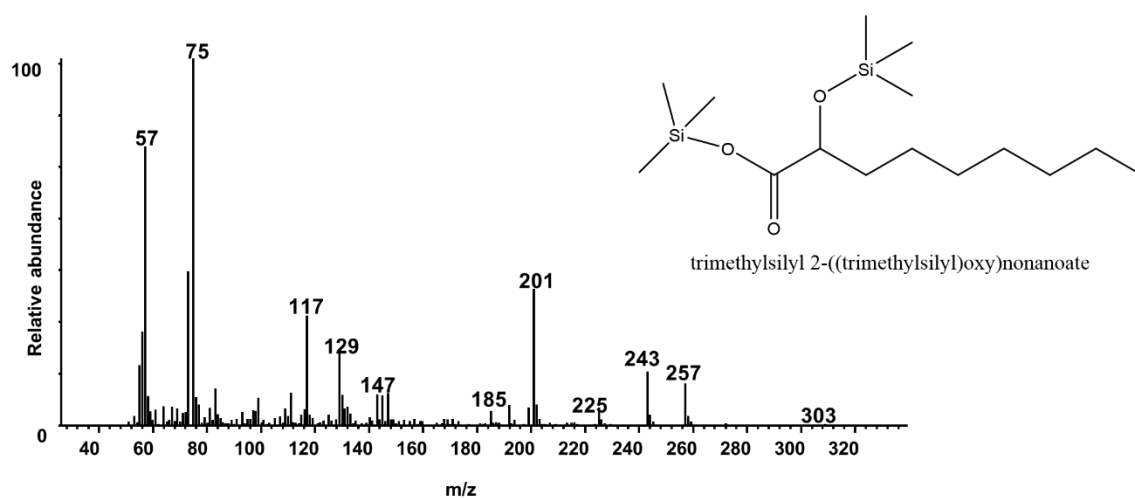


Figure S13. Mass spectrum of trimethylsilyl 2-((trimethylsilyl)oxy)nonanoate obtained with GC-MS.

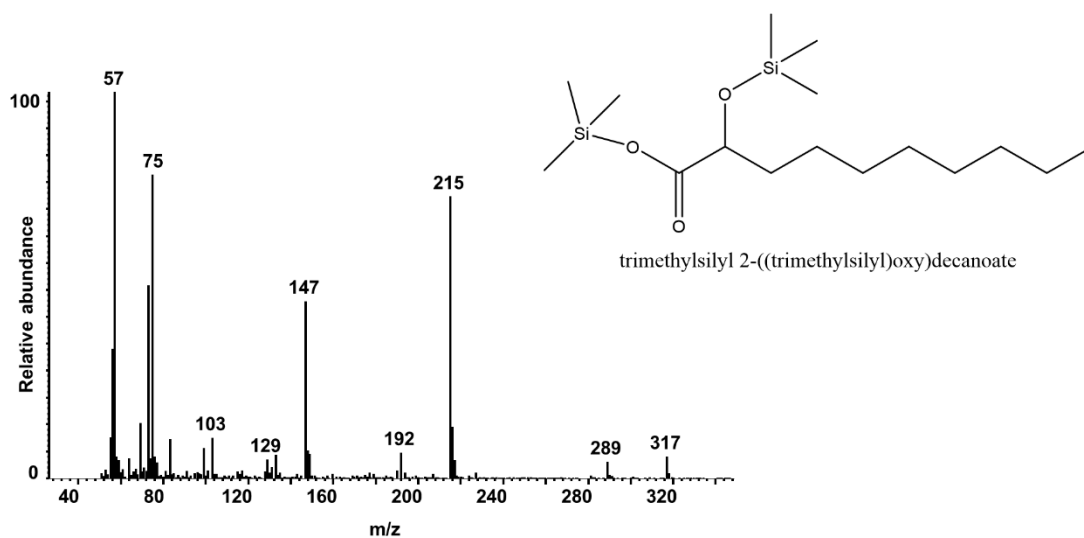


Figure S14. Mass spectrum of trimethylsilyl 2-((trimethylsilyl)oxy)decanoate obtained with GC-MS.

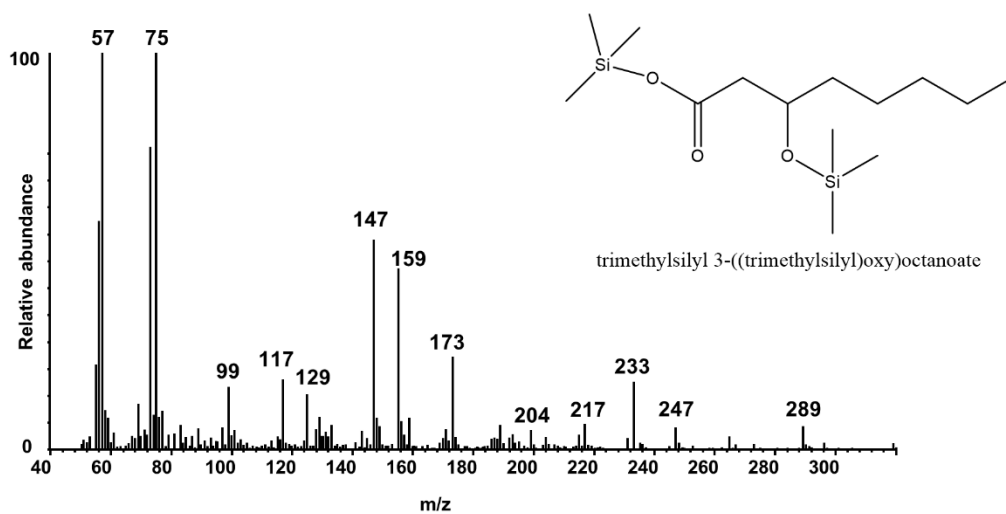


Figure S15. Mass spectrum of trimethylsilyl 3-((trimethylsilyl)oxy)octanoate obtained with GC-MS.

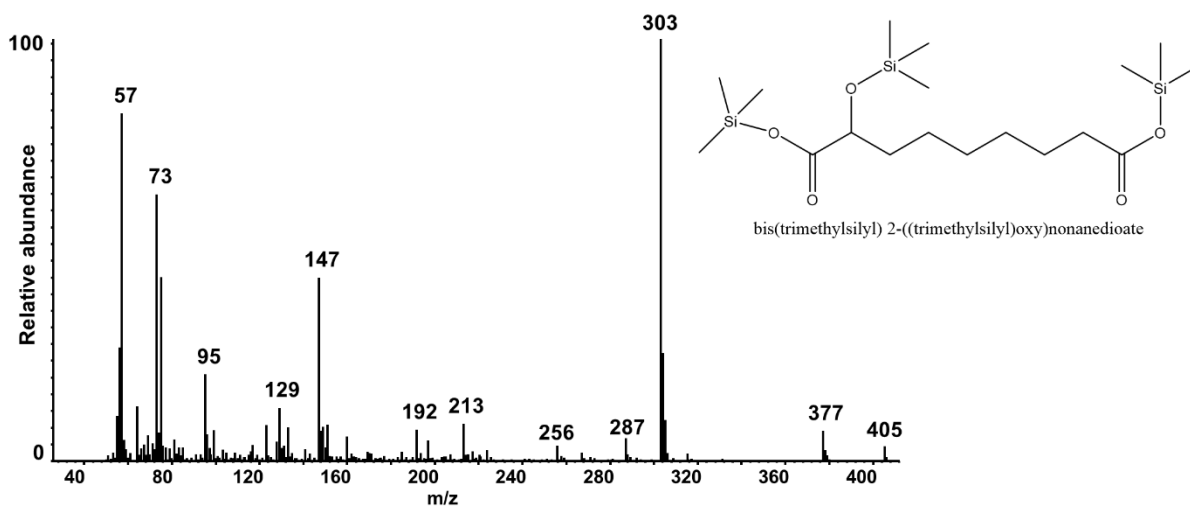


Figure S16. Mass spectrum of bis(trimethylsilyl) 2-((trimethylsilyl)oxy)nonanedioate obtained with GC-MS.

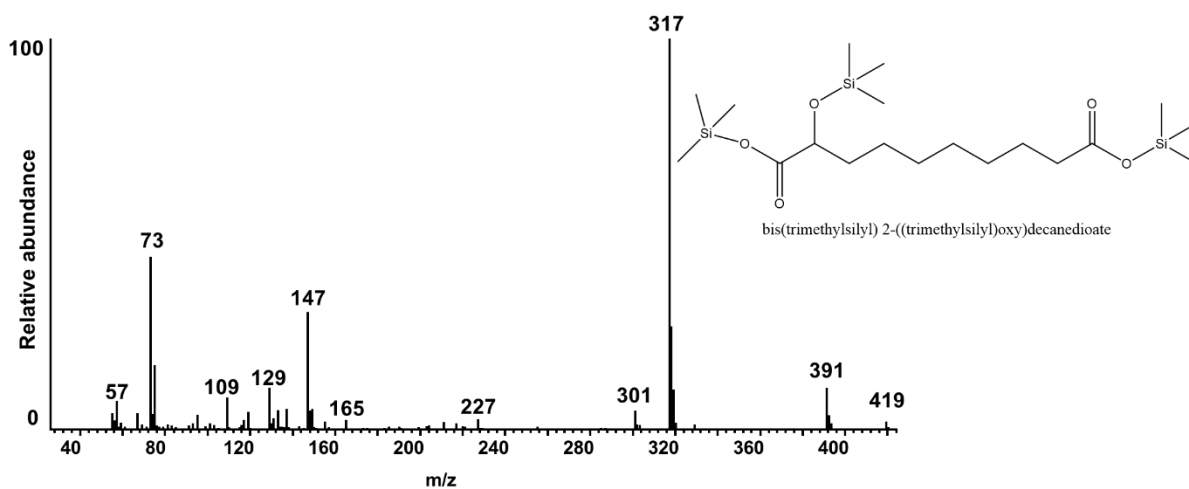


Figure S17. Mass spectrum of bis(trimethylsilyl) 2-((trimethylsilyl)oxy)decanedioate obtained with GC-MS.

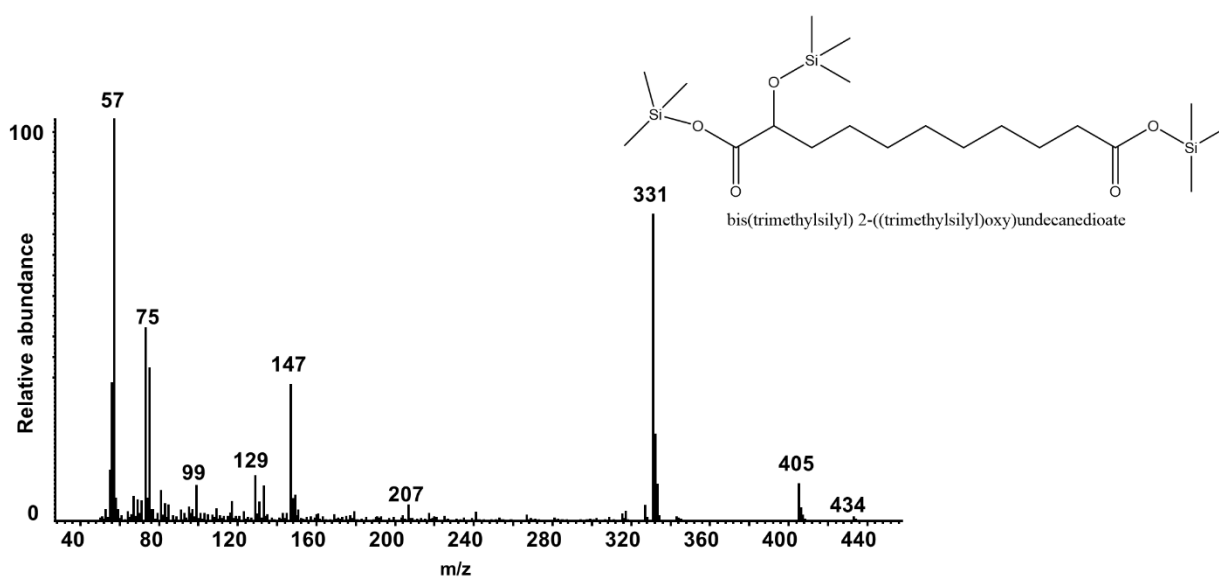


Figure S18. Mass spectrum of bis(trimethylsilyl) 2-((trimethylsilyl)oxy)undecanedioate obtained with GC-MS.

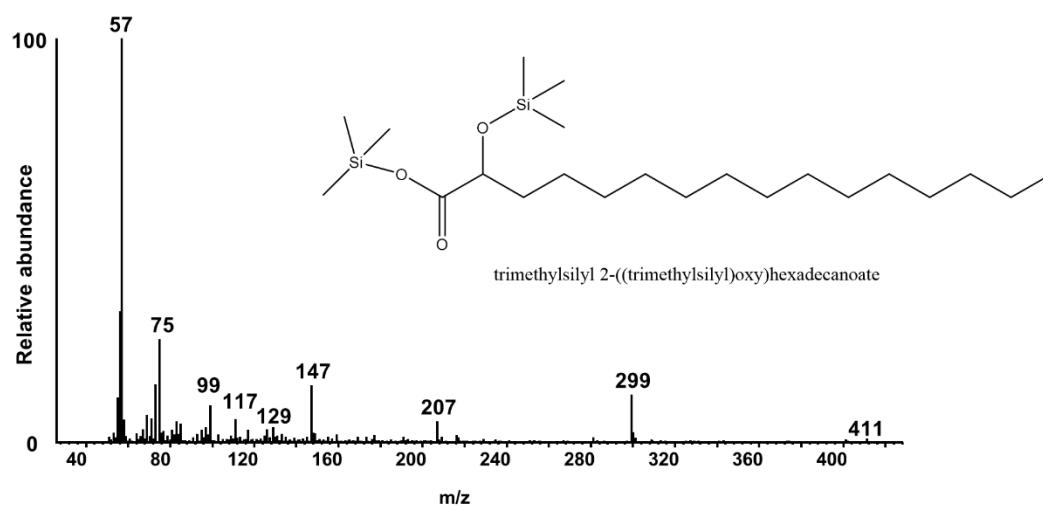


Figure S19. Mass spectrum of trimethylsilyl 2-((trimethylsilyl)oxy)hexadecanoate obtained with GC-MS.

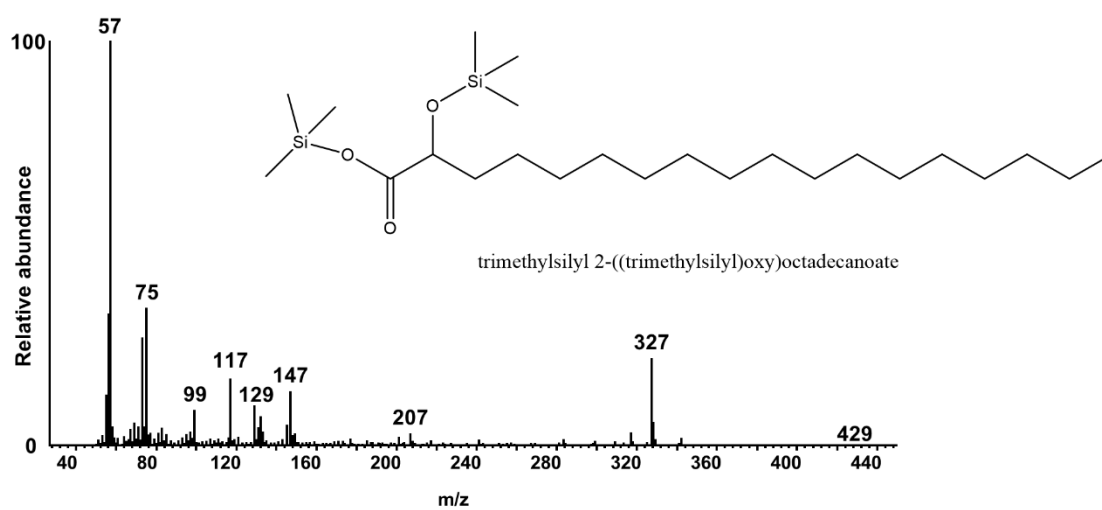


Figure S20. Mass spectrum of trimethylsilyl 2-((trimethylsilyl)oxy)octadecanoate obtained with GC-MS.

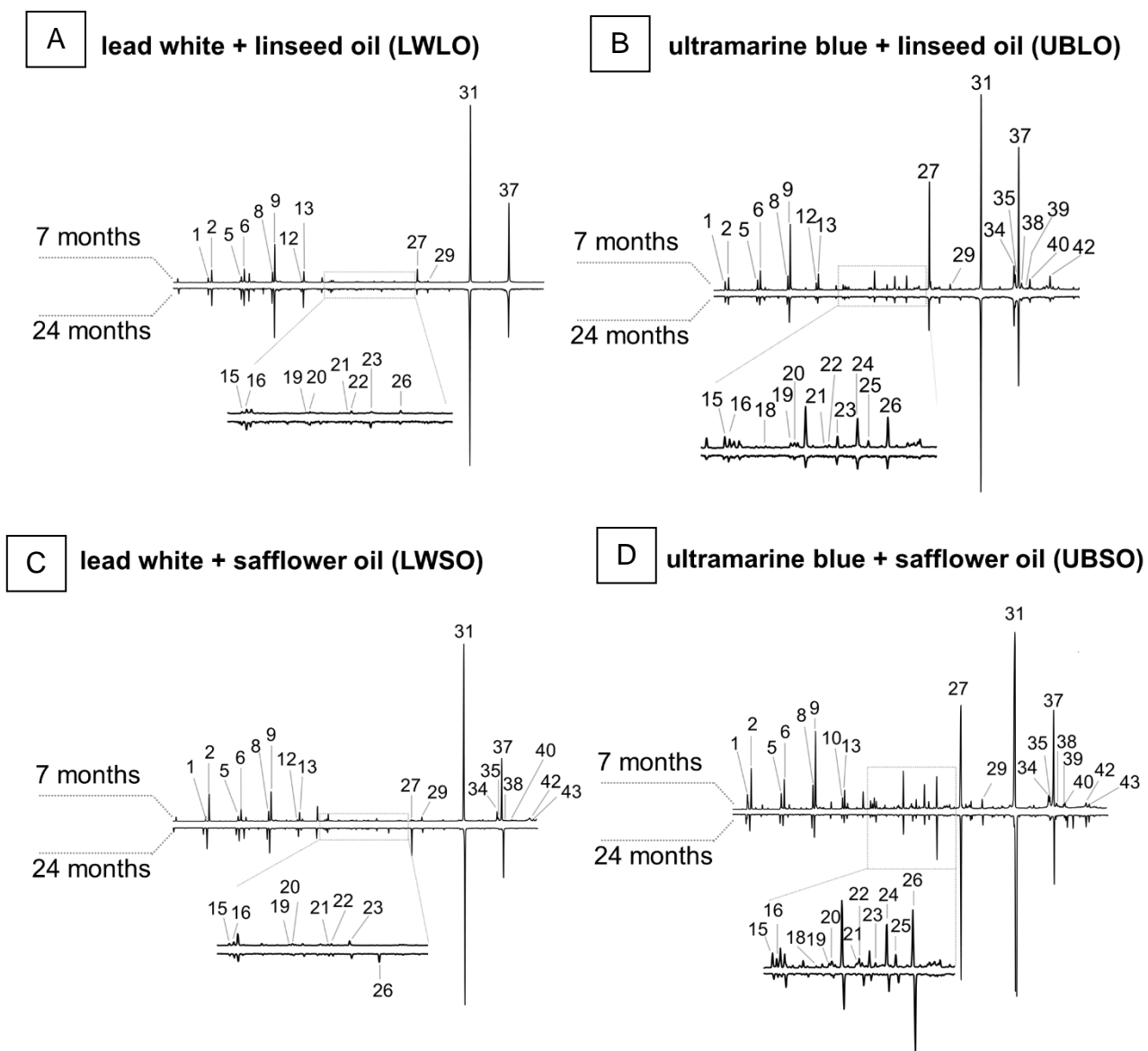


Figure S21. Extracted ion pyrograms of m/z 129 of A) LWLO, B) LWSO, C) UBLO and D) UBSO paints after 7 and 24 months of natural ageing. The peak numbers refer to the list reported in **Table S3**.

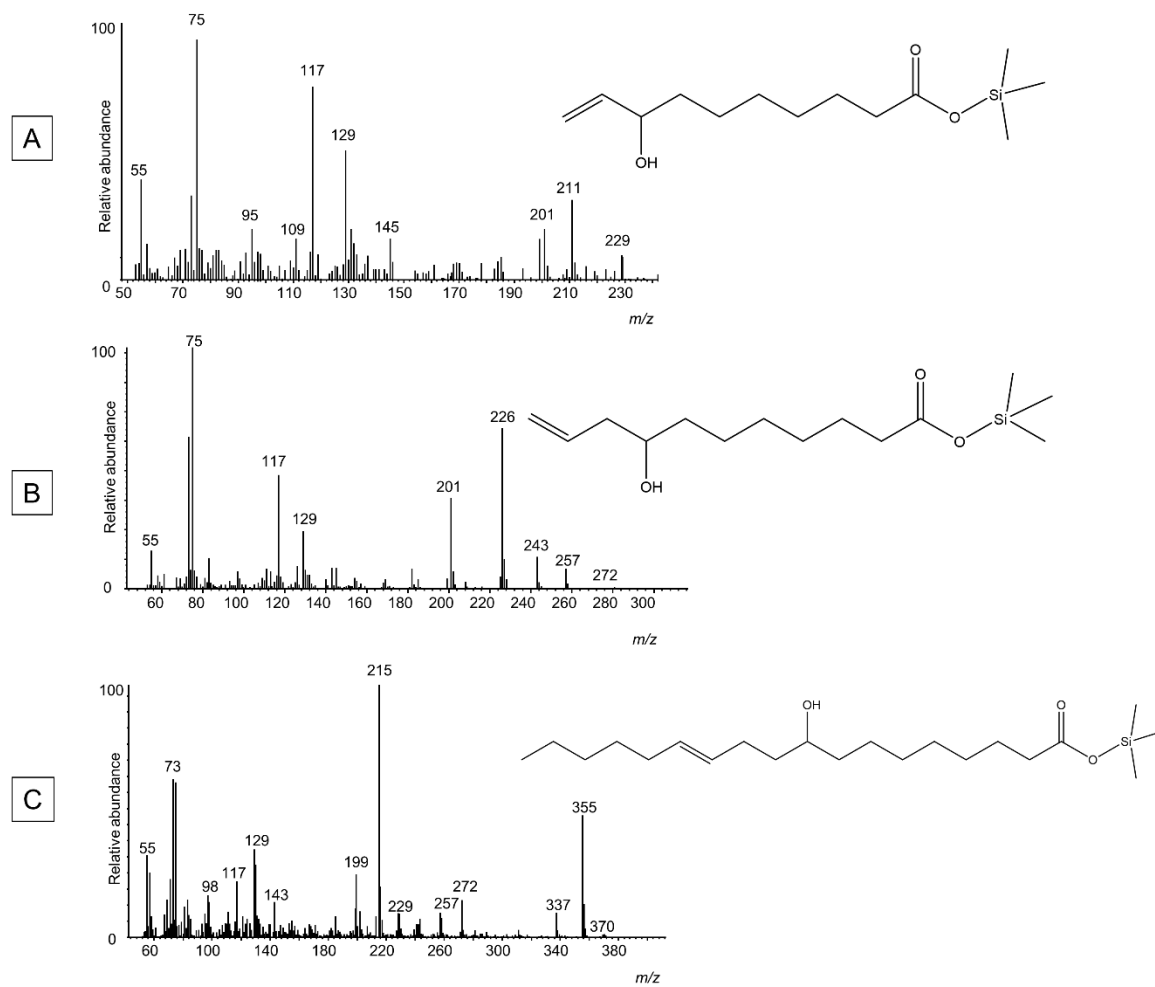


Figure S22. Mass spectra attributed to A) 8-hydroxydec-9-enoic acid, B) 8-hydroxyundec-10-enoic acid and C) 9-hydroxyoctadec-12-enoic acid.