

## Supporting Information

# Discoloration of Historical Plastic Objects: New Insight into the Degradation of $\beta$ -Naphthol Pigment Lakes

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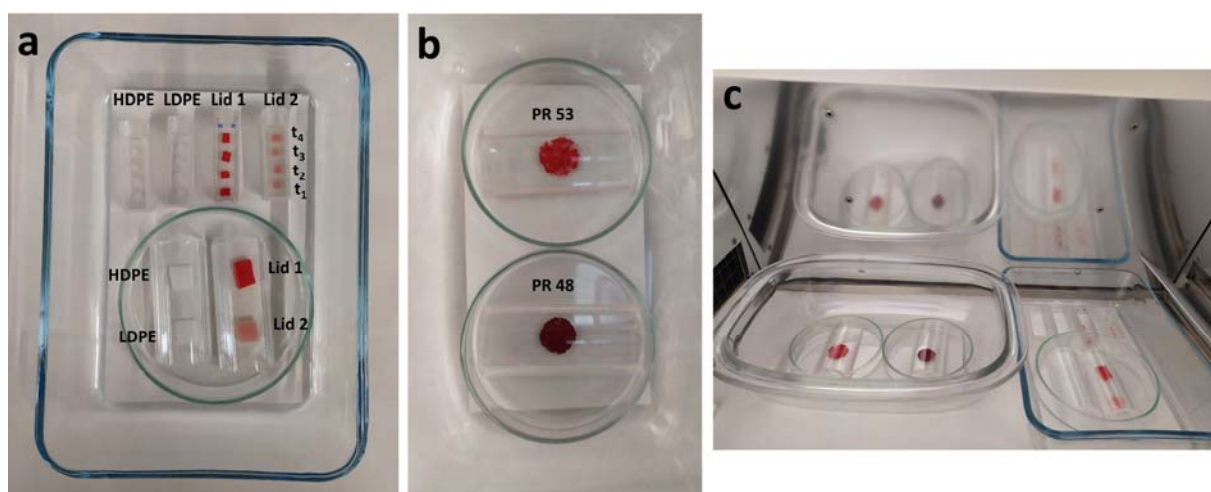
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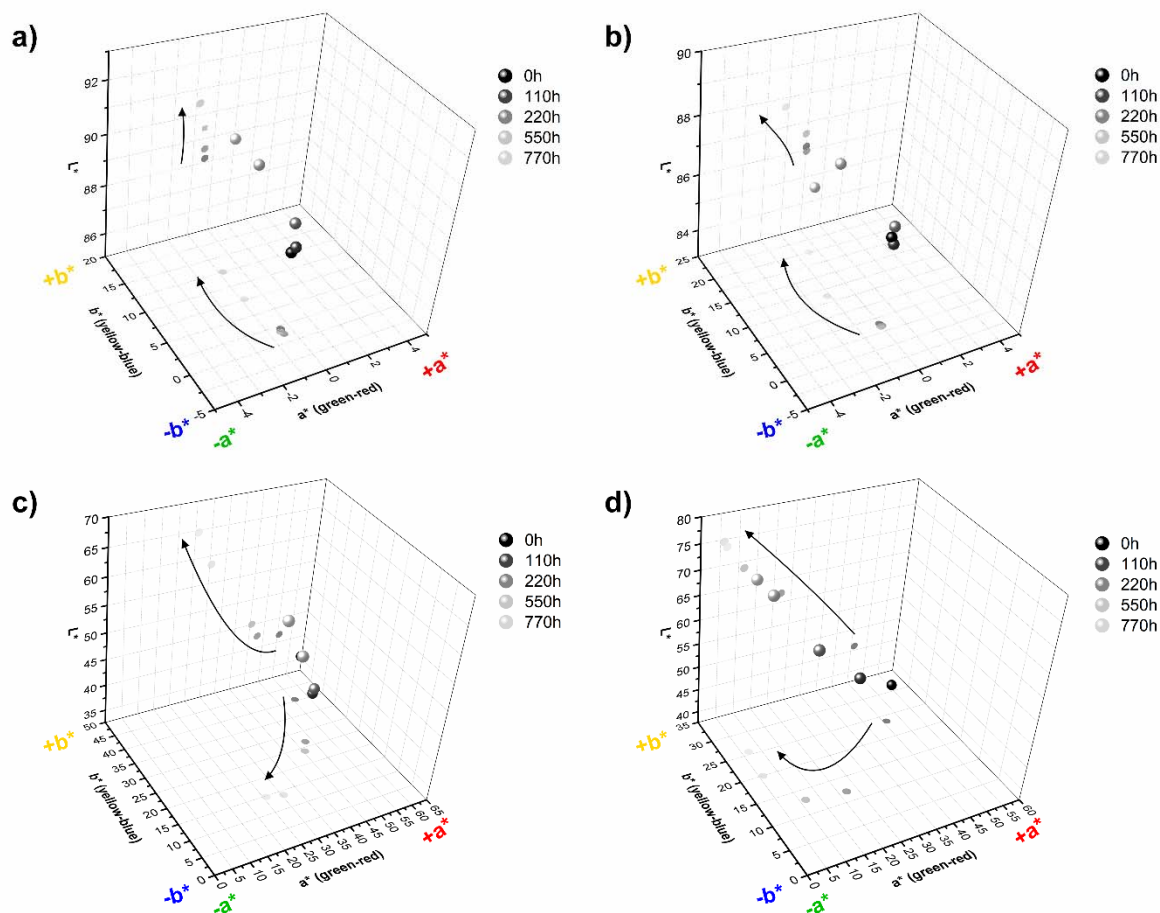
## Colorimetric measures

During color measurement significant differences with the 0h are indicated for both PE reference samples and historical lids. In detail, stepwise increase in the positive  $b^*$  values of HDPE and LDPE samples was observed indicative of yellowing (**Figure S2a,b**). The historical lids share the same tendency with their positive  $a^*$  and  $b^*$  coordinates decreasing towards more achromatic values as  $L^*$  increases (**Figure S2c,d**). This trend is easily explained because the red pigments of the historical samples faded.  $L^*a^*b^*$  coordinates and total color variation between 0h and 770h of irradiation are reported in **Table S3**. The most dramatic color change was observed for lid 1 and 2 ( $\Delta E^*_{ab} > 45$ ). Lid 2 was partially discolored before irradiation, and its color faded completely with the photoaging (**Figure S3**). Interestingly, it presents fading until 220h while after the only polymer contributes to color change with yellowing symptoms (**Figure S2d**).

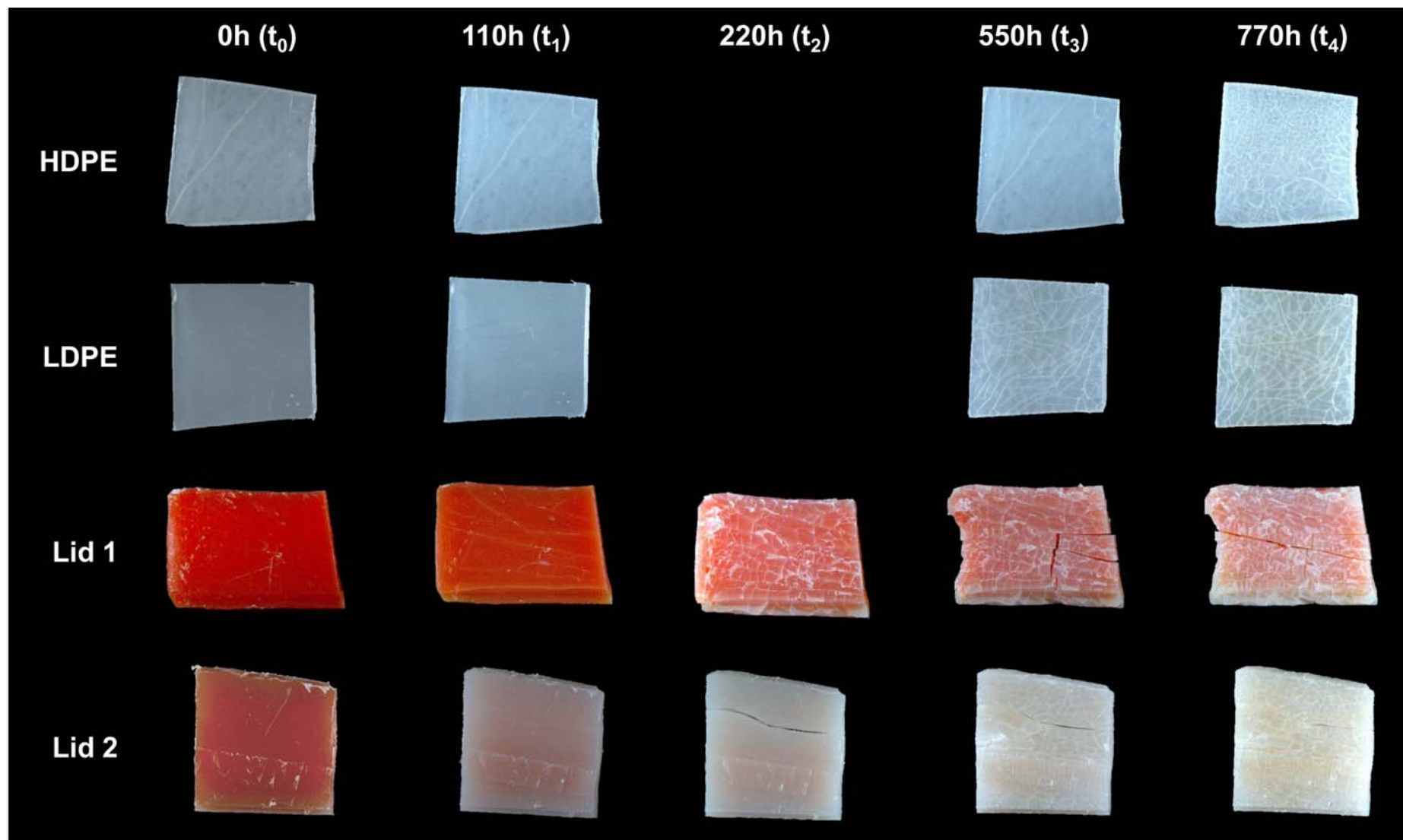
## Figures



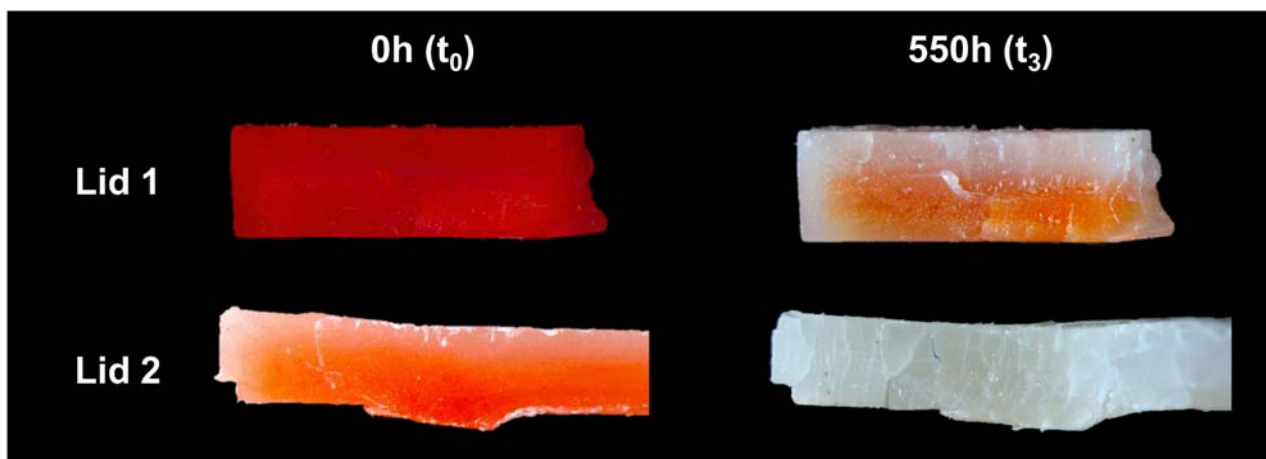
**Figure S1.** Arrangement of samples during the aging experiment. a) historical and polymer reference samples, b) pigment powders, c) all samples inside of the chamber.



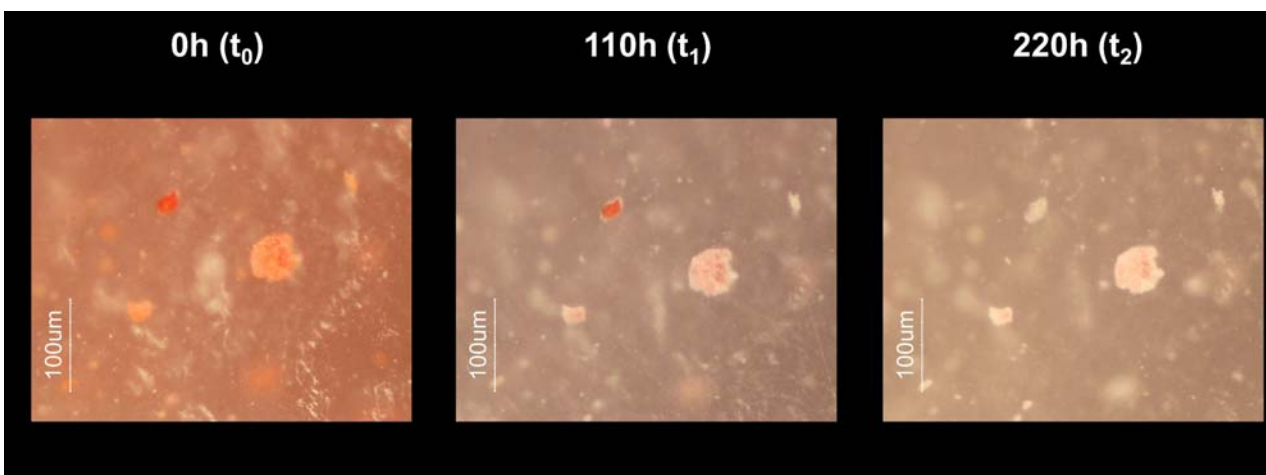
**Figure S2.**  $L^*$ ,  $a^*$ ,  $b^*$  values in 3-dimensional CIELab76 Color Space during aging: (a) HDPE, (b) LDPE, (c) lid 1, (d) lid 2. Projections of the points along the  $L^*$  vertical axis and  $a^*$  and  $b^*$  perpendicular horizontal axes are also reported. The arrows define the color change over time.



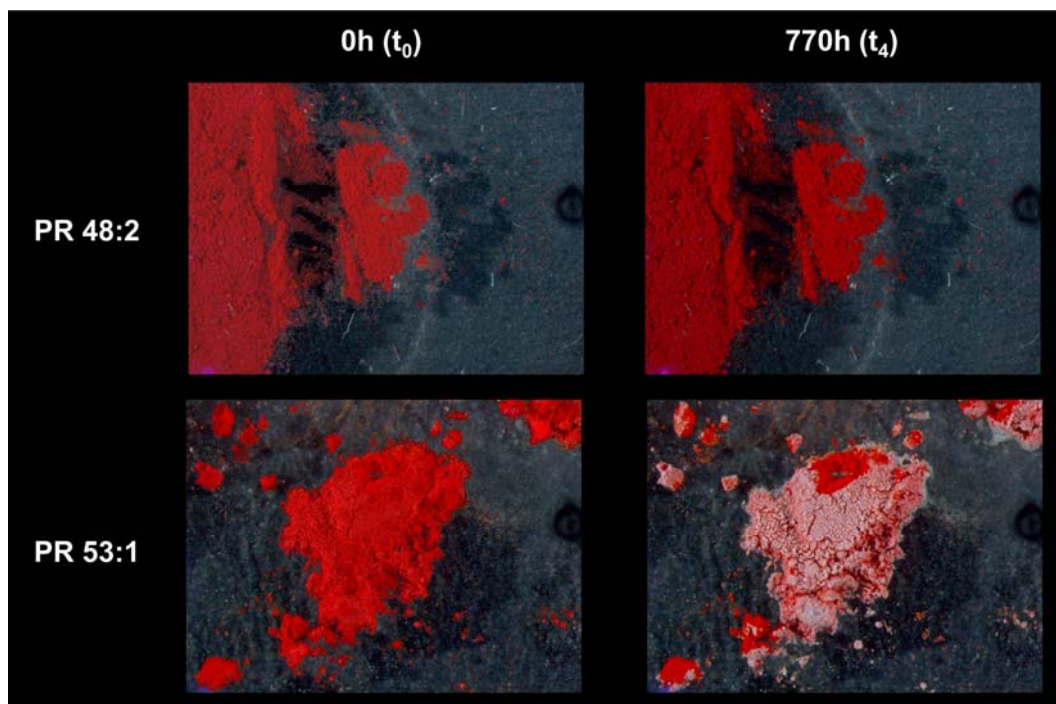
**Figure S3.** Stereomicroscope images of the plastic samples during the aging (25x). The pictures show the exposed areas.



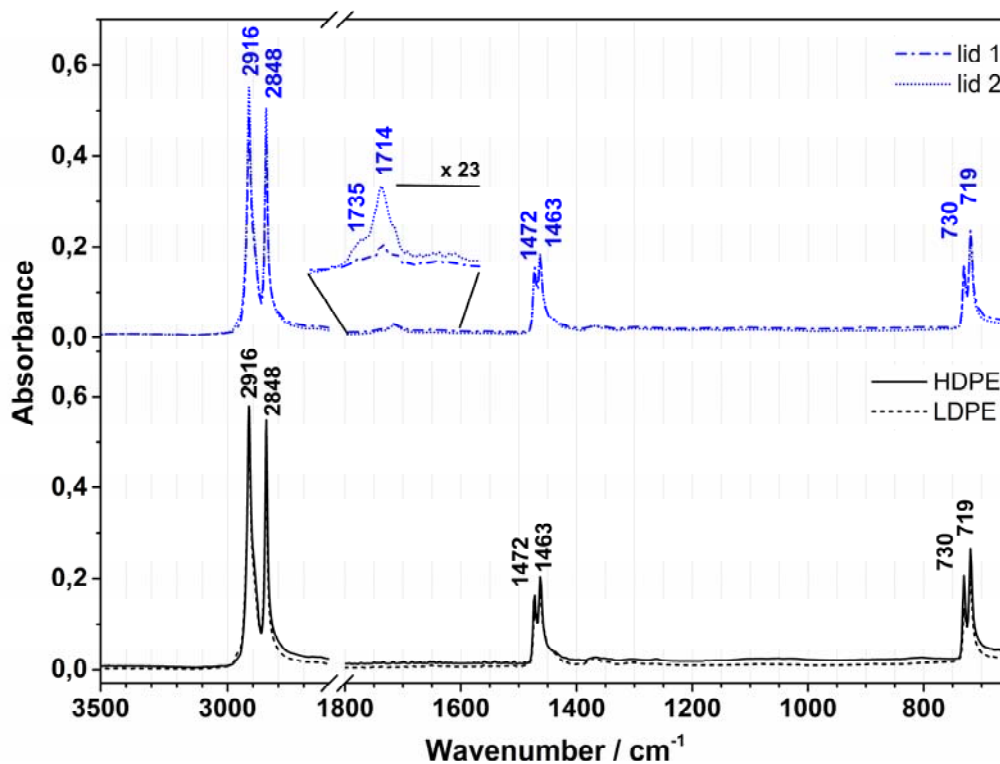
**Figure S4.** Stereomicroscope images taken from the side of the lids 1 and 2 at 0h and 550h (ca.1 mm thickness). The exposed areas correspond to the upper part of the sample.



**Figure S5.** Microscopy images of the red particles/aggregates dispersed in the polymeric matrix under reflected visible light (dark field) of lid 2 sample. Images were collected directly from the sample in situ.

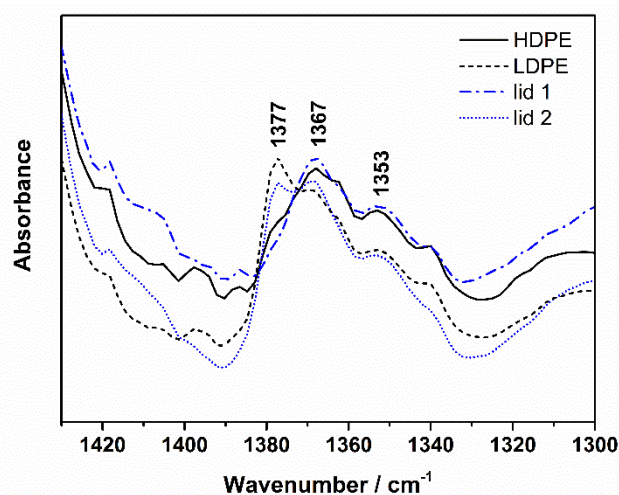


**Figure S6.** Stereomicroscope images of the pigment powders at 0h and 770h.

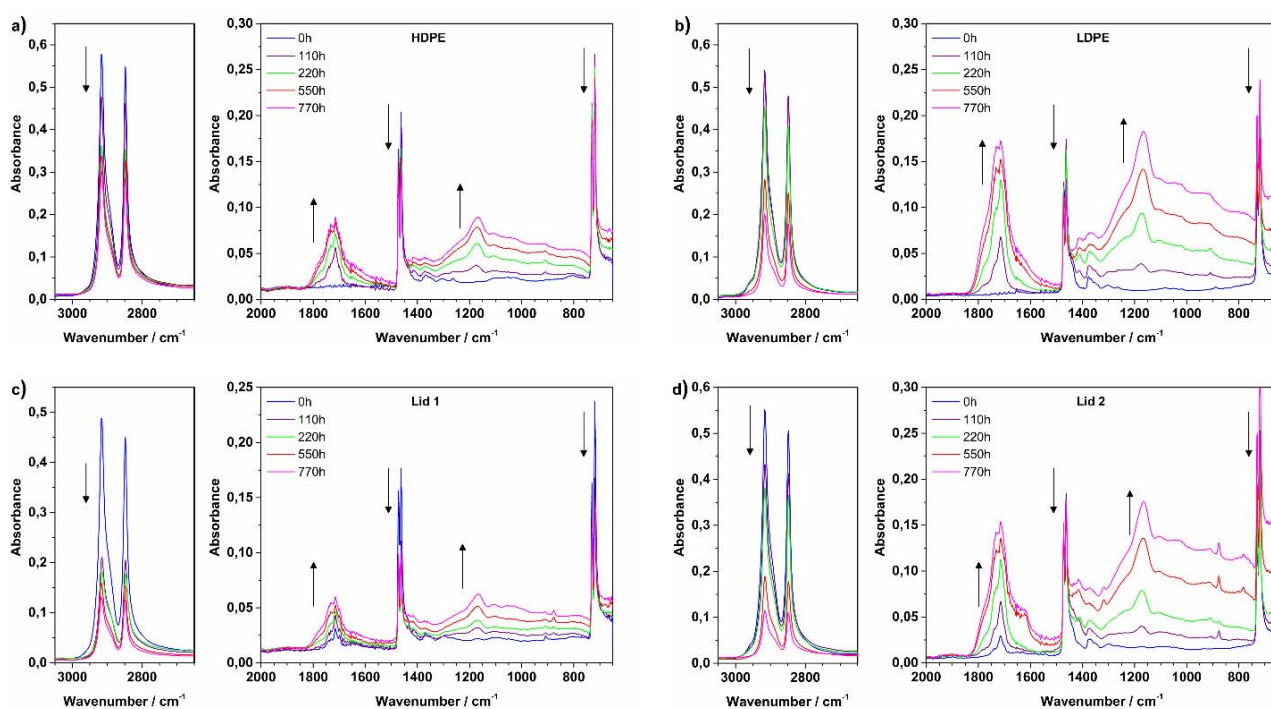


**Figure S7.** ATR-FTIR spectra of lid 1 and lid 2 samples (top, blue lines). Vibrational spectra of the polymer references HDPE and LDPE are reported for comparison (bottom, black lines).

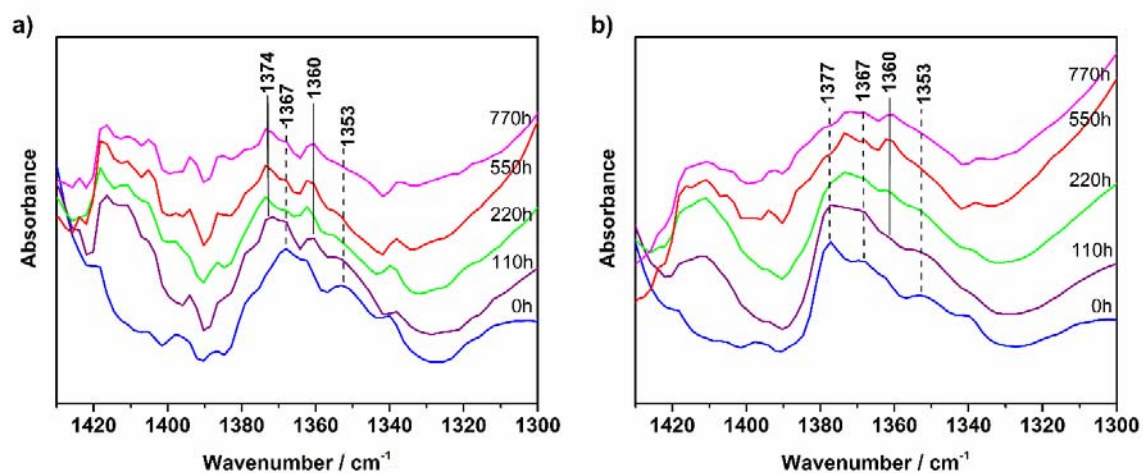




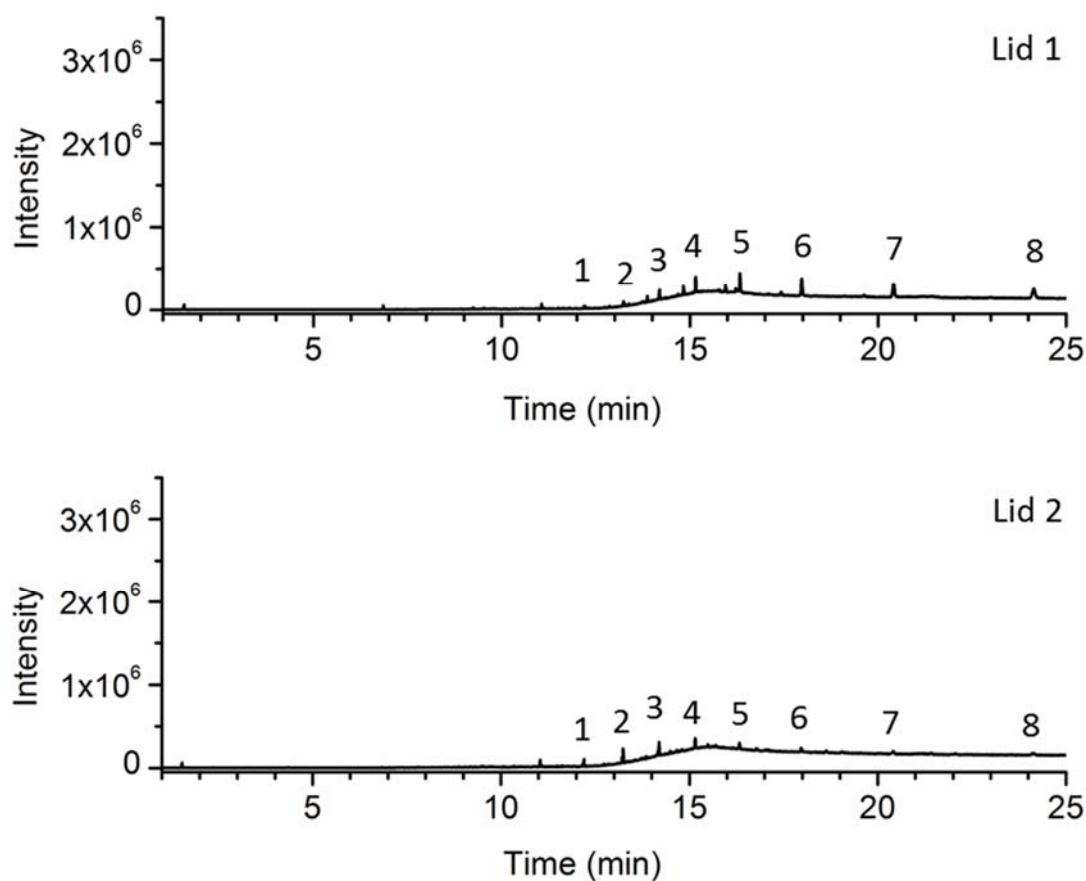
**Figure S8.** ATR-FTIR spectra of HDPE, LDPE, lid 1 and lid 2 samples at  $t_0$  (detail of the interval 1300–1430  $\text{cm}^{-1}$ ).



**Figure S9.** ATR-FTIR spectra of HDPE (a), LDPE (b), lid 1 (c) and lid 2 (d) samples over aging. The arrows' direction indicates the increase or decrease of IR bands intensity with increasing aging.



**Figure S10.** ATR-FTIR spectra of the (a) HDPE and (b) LDPE with magnification of the 1300–1430 cm<sup>-1</sup> range over aging.

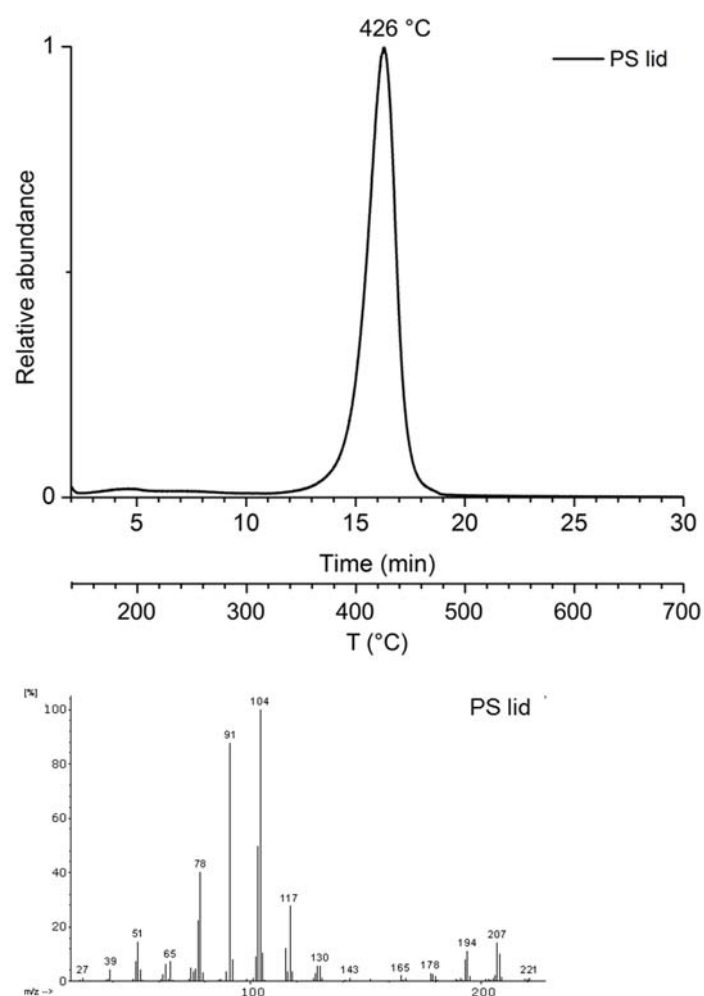


**Figure S11.** TD-chromatograms of lid 1 (up) and lid 2 (bottom). See **Table 2** for peak identification.

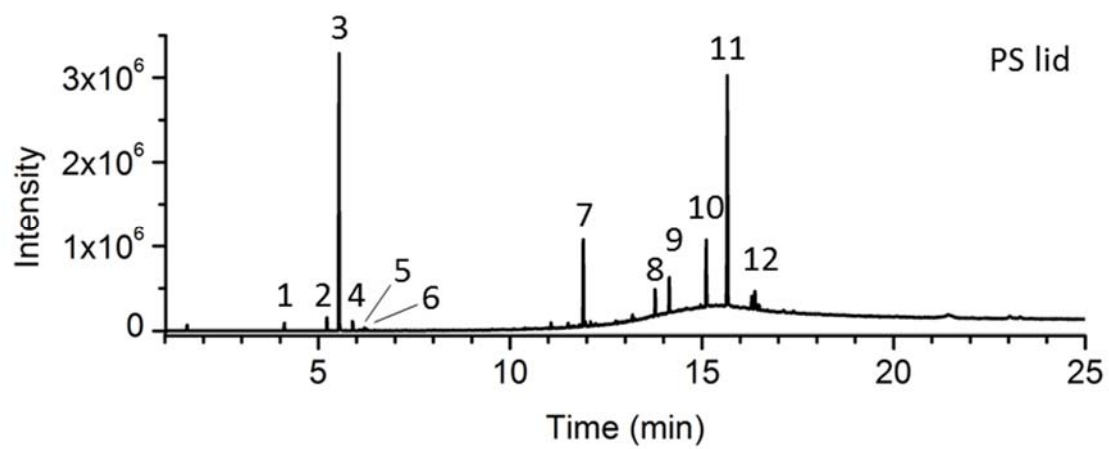




**Figure S12.** Historical sample presenting PR 53 not discolored. PS lid 3 on the bottom.



**Figure S13.** Top: normalized EGA-MS curves of the red PS lid 3 and bottom: related average mass spectrum.



**Figure S14.** TD-chromatogram of the red PS lid 3. For the peaks identification, see **Table S5**.

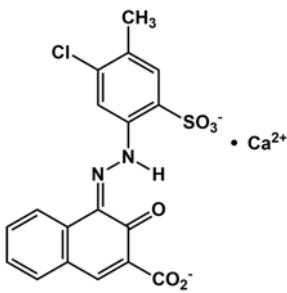
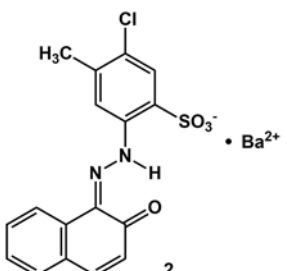
## Tables

**Table S1.** Summary of multi-analytical analysis of polymer, red pigments and white pigments / fillers from [1].

Historical sample	Plastic polymer	Elemental composition	Red organic pigments	Red inorganic pigments	White pigments / fillers
Lid 1	PE	Ti, Ca, Zn, Fe, K, Cl, Si	PR 48:2	PR 101	-
Lid 2	PE	Ti, Ca, Zn, Fe, Ba	PR 53:1	-	PW (R)

Note. PR: Pigment Red, PW: Pigment White, R: rutile crystalline form

**Table S2.** Molecular structures and acronyms of the synthetic organic pigments studied.

C.I. Generic name	Common name	C.I. Constitution number	Class <sup>a</sup>	Structure <sup>b</sup>
PR 48:2	Calcium Red 2B	15865:2	BONA pigment lake	
PR 53:1	Lake Red C	15585:1	$\beta$ -naphthol pigment lake	

Note. PR: Pigment Red, <sup>a</sup> Classification of organic pigments based on the chemical structure as presented in [2]. <sup>b</sup> Colorants based on 1-aryldiazene-2-naphthol skeleton, such as  $\beta$ -naphthol pigments, undergo a tautomeric rearrangement between hydrazone/keto and azo/enol forms. Molecular structures of the organic red pigment are depicted in the hydrazone/keto form which is accepted as the major tautomer [2].

**Table S3.** Colorimetric coordinates of HDPE, LDPE, lid 1 and lid 2 at each irradiation time. Total color difference  $\Delta E_{ab}^*$  (CIE1976),  $\Delta E_{00}$  (CIEDE2000) between 0h and 770h are reported.

	HDPE			LDPE			Lid 1			Lid 2		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
0h (t <sub>0</sub> )	88.17	-0.41	2.04	86.14	-0.01	3.92	41.55	55.61	40.56	46.02	45.99	23.65
±	0.12	0.01	0.02	0.05	0.01	0.02	0.04	0.06	0.07	0.05	0.20	0.08
110h (t <sub>1</sub> )	88.57	-0.44	1.28	85.96	0.03	3.53	42.37	47.87	26.59	61.87	22.12	12.04
±	0.06	0.02	0.01	0.01	0.01	0.01	0.03	0.15	0.23	0.05	0.01	0.06
220h (t <sub>2</sub> )	89.42	-0.51	1.67	86.60	-0.06	3.40	45.08	45.54	23.89	68.67	11.51	12.92
±	0.51	0.01	0.03	0.07	0.01	0.01	0.02	0.05	0.06	0.29	0.10	0.06
550h (t <sub>3</sub> )	90.43	-0.85	7.65	87.69	-1.14	11.20	58.45	30.51	13.74	74.59	5.97	19.97
±	0.80	0.01	0.04	0.25	0.02	0.04	0.09	0.08	0.16	0.24	0.01	0.32
770h (t <sub>4</sub> )	90.45	-0.81	12.54	85.44	-0.41	20.07	64.62	25.87	14.74	73.47	6.81	25.67
±	0.08	0.04	0.15	0.16	0.01	0.04	0.06	0.05	0.14	0.28	0.04	0.97
$\Delta E_{ab}^*$			<b>10.75</b>			<b>16.17</b>			<b>45.64</b>			<b>47.88</b>
$\Delta E_{00}$			<b>8.04</b>			<b>10.50</b>			<b>25.74</b>			<b>33.94</b>

**Table S4.** List of pyrolysis products from the pigment powders PR 48:2 and PR 52:1 before (0h) and after aging (770h). Characteristic ions in mass spectra: molecular weight (M<sub>w</sub>) bold, base peak underlined.

tr / min	Compound	m/z	PR48 (0h)	PR48 (770h)	PR53 (0h)	PR53 (770h)
1.56	CO <sub>2</sub>	28, <u><b>44</b></u>	x	x	x	x
1.60	Sulfur dioxide	32, 48, <u><b>64</b></u>	x	x	x	x
2.73	Benzene	39, 51, <u><b>78</b></u>	x	x	x	x
5.27	Styrene	51, 78, <u><b>104</b></u>	x	x	x	x
5.99	Toluene, o-chloro	39, 63, <u><b>91</b></u> , <b>126</b>	x	x	x	x
6.24	Phenol	39, 66, <u><b>94</b></u>		x		x
6.25	Aniline	39, 66, <u><b>93</b></u>	x		x	
6.32	Benzonitrile	50, 76, <u><b>103</b></u>	x	x	x	x
7.05	Indene	39, 63, 89, 115, <u><b>116</b></u>	x	x	x	x
7.26	m-tolunitrile	39, 63, 90, <u><b>117</b></u>	x	x		
7.27	m-cresol	51, 77, 90, <u><b>107</b></u> , <b>108</b>			x	x
7.30	p-toluidine	39, 53, 77, 89, <u><b>106</b></u> , <b>107</b>	x	x		
7.36	m-toluidine	39, 53, 77, 89, <u><b>106</b></u> , <b>107</b>			x	x
8.46	Quinoline	51, 63, 76, 102, <u><b>129</b></u>	x	x	x	x
8.51	Naphthalene	51, 63, 102, <u><b>128</b></u>	x	x	x	x
8.59	m-Chloroaniline	39, 65, 92, <u><b>127</b></u>	x	x		
9.09	3-Chloro-4-methylbenzonitrile	39, 63, 89, <u><b>116</b></u> , <b>151</b>	x	x		
9.36	Phenol, 3-chloro-4-methyl	39, 51, 77, <u><b>107</b></u> , <b>142</b>	x	x		
9.38	Phenol, 4-chloro-3-methyl	39, 51, 77, <u><b>107</b></u> , <b>142</b>			x	x
9.49	p-Toluidine, 3-chloro-	51, 77, 106, <u><b>140</b></u> , <b>141</b>	x	x		

9.56	m-Toluidine, 4-chloro	51, 77, <u>106</u> , 140, <b>141</b>			x	x
9.67	Phthalic anhydride	50, 76, <u>104</u> , <b>148</b>		x		x
9.95	1H-Indene-1,3(2H)-dione	50, 76, 104, <b>146</b>		x		
10.52	Similar to 4-Cyanocinnoline	50, 74, 100, <u>127</u> , <b>155</b>	x	x		
10.90	Phthalimide	50, 76, 104, <u>147</u>		x		x
11.29	2,4-di-tert-Butylphenol	57, 163, <u>191</u> , <b>206</b>	x			
11.47	$\beta$ -Naphthol	89, 115, <u>144</u>	x	x	x	x
11.50	Similar to 4-quinolinecarboxaldehyde	51, 75, 101, 129, <u>157</u>	x	x		
11.69	Unidentified	114, 140, <u>169</u>	x	x		
11.70	Similar to 2-naphthalenamine	71, 115, <u>143</u>			x	x
12.48	Unidentified	114, 154, <u>183</u>	x	x		
13.26	2-Naphthalenol, 1-amino	51, 77, 103, 130, <u>159</u>	x	x	x	x
15.76	Unidentified	189, 219, <u>234</u>			x	x
16.16	Unidentified	94, 189, <u>218</u>	x	x		
17.05	Similar to 2H-phenanthro[9,10-b]pyran	101, 202, <u>232</u>			x	x
17.13	Unidentified	202, <u>232</u>	x	x		
17.19	Unidentified	115, 205, <u>268</u>			x	x
17.50	Unidentified	189, 202, 218, 233, <u>268</u>	x	x	x	x
17.72	Unidentified	94, 189, <u>252</u>	x	x	x	x
17.83	Unidentified	76, 104, 192, 227, 236, <u>271</u>		x		
17.88	Unidentified	114, <u>245</u>	x	x	x	x
18.67	Unidentified	122, <u>244</u> , 266	x	x		
18.75	9-Chloro-5,6-dihydronaphthol[1,2-c]cinnoline	101, 202, 231, <u>266</u>			x	x
18.77	8-Chloro-5,6-dihydronaphthol[1,2-c]cinnoline	101, 202, 231, <u>266</u>	x	x		
19.59	Unidentified	115, 127, 241, <u>270</u>			x	x
20.22	Unidentified	121, 243, <u>278</u>	x	x		
21.20	Unidentified	119, 239, <u>268</u>			x	x
21.85	Unidentified	200, 231, <u>330</u>			x	x

**Table S5.** Main volatile organic compounds detected in the red PS lid 3 (characteristic ions in mass spectra: molecular weight,  $M_w$ , in bold and base peak underlined). Additives are marked in *italic*.

Peak number	Compound	$m/z$
1	Toluene	39, 65, 89, <u>91</u> , <b>92</b>
2	Ethylbenzene	39, 51, 65, 77, <u>91</u> , <b>106</b>
3	Styrene	39, 51, 63, 78, <u>104</u>
4	Isopropylbenzene	39, 51, 79, 91, <u>105</u> , <b>120</b>
5	Allylbenzene	39, 51, 65, 78, 91, 103, <u>117</u> , <b>118</b>
6	$\alpha$ -Methylstyrene	39, 51, 78, 91, 103, 117, <u>118</u>

7	3-Butene-1,3-diyl dibenzene (styrene dimer)	39, 51, 65, 77, <u>91</u> , 104, 115, 130, 193, <b>208</b>
8	<i>Drometrizol</i>	39, 51, 66, 78, 93, 154, 168, 196, <u>225</u>
9	<i>Palmitic acid butyl ester</i>	29, 43, <u>56</u> , 73, 97, 129, 185, 239, 257, <b>312</b>
10	<i>Stearic acid butyl ester</i>	29, 43, <u>56</u> , 73, 97, 129, 185, 241, 267, 285, <b>340</b>
11	5-Hexene-1,3,5-triyltribenzene (styrene trimer)	65, 77, <u>91</u> , 117, 194, 207, <b>312</b>
12	Isomers of styrene trimer	65, 77, 91, <u>129</u> , 207, <b>312</b>

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## References

- [1] Angelin, E. M.; França de Sá, S.; Picollo, M.; Nevin, A.; Callapez, M. E.; Melo, M. J. The identification of synthetic organic red pigments in historical plastics: Developing an in situ analytical protocol based on Raman microscopy. *J Raman Spectrosc.* **2021**, 52, 145-158. DOI: [10.1002/jrs.5985](https://doi.org/10.1002/jrs.5985)
- [2] Hunger, K.; Schmidt M. U. *Industrial Organic Pigments: Production, Crystal Structures, Properties, Applications*, 4th ed.; Wiley-VCH: Weinheim, Germany, 2018.