PYROLYSIS-GC/MS OF MODERN INKS: THE FELT-TIP PENS USED BY LINA BO BARDI

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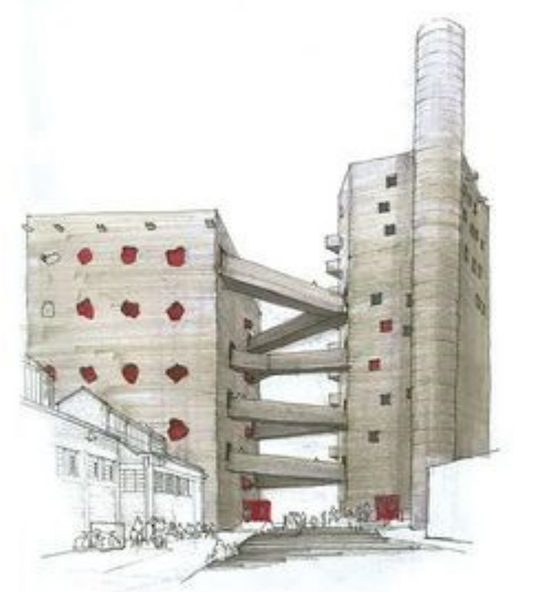


Lina Bo Bardi, SESC Pompeia - São Paulo, Brasil, sketch

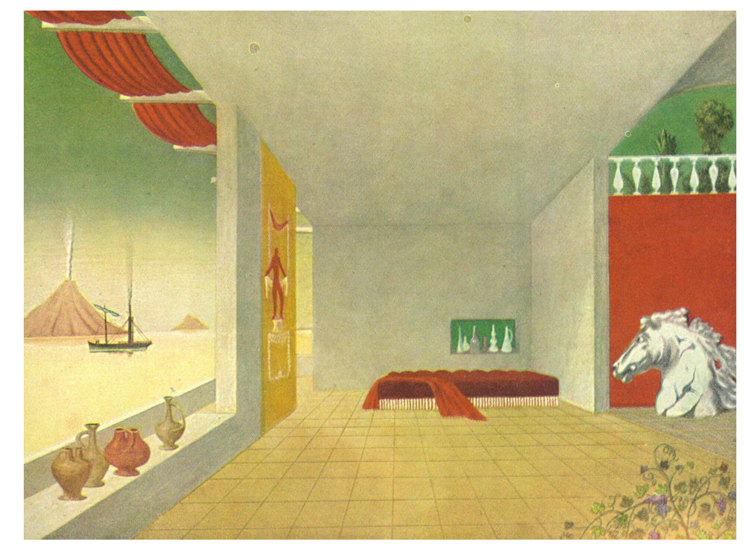
Investigated felt/tip pens used by Lina Bo Bardi

Lina Bo Bardi (1914, Rome (Italy) - 1922, São Paulo (Brazil)) was a brazilian modernist architect, industrial designer, historic preservationist, journalist, and activist whose work defied conventional categorization. Many sketches, drawings, copies, architectural drawings and other technical designs have been realized with felt-tip pens. Unfortunately, the inks are usually very sensitive to light and chemical agents and the exact knowledge of their composition may be important to define the optimal conservation treatment and/or storage conditions.

A multi-technique approach based on scanning electron microscopy, X-ray fluorescence, infrared spectroscopy, Raman spectroscopy [1] and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) has been exploited to identify the chemical composition of twenty felt-tip pens used by the architect.

In this contribution the Py-GC/MS[1] data are presented. The pyrograms of the felt-tip pens allowed the identification of the class, subclass or of individual dyes. In particular, triarylmethane, xanthene and indigoid dyes could be efficiently detected. For many dyes unpublished characteristic pyrolysis products are proposed. However, in the pyrograms of the felt-tip pens containing nigrosine dyes only few non-specific pyrolysis products could be detected.

[1]Py/GC-MS was performed with a Pyrojector II (SGE) pyrolyser kept at a temperature of 600°C. GC (Clarus 680 -Perkin Elmer) oven program: 40(4)-15-280(10)- Elite-5MS (30 m x 0.25 mm i.d., 0.25 µm). Helium was used as carier gas. Injector, transfer line and ion source temperatures were set at 280, 290 and 250°C, respectively. MS (Clarus SQ 8T -Perkin Elmer): 70 eV; 45-450 *m/z*.



Lina Bo Bardi, house at the seaside, sketch

Lina Bo Bardi, Bowl chair, sketch

Triarylmethane dyes

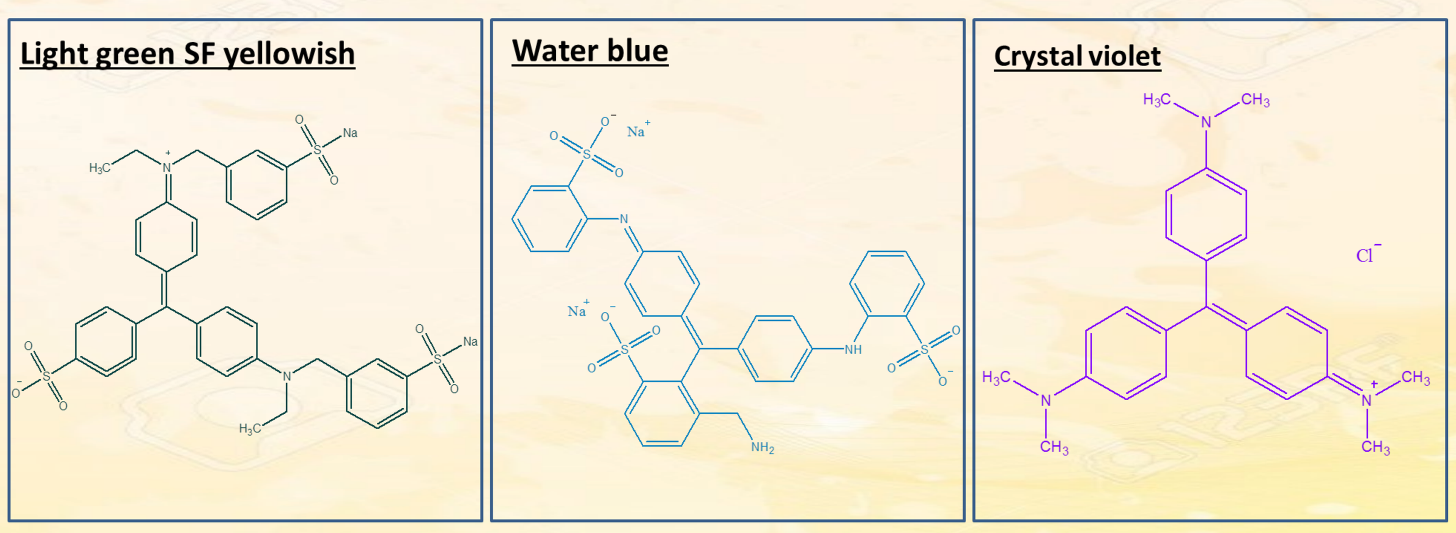


Fig.1 Chemical structures of three triarylmethane dyes: ligth SF yellowish, water blue and crystal violet

Tab.1 Main pyrolysis products for the triarylmethane dyes

N.	RT (min)	Compounds	main *m/z*
1	1.3	sulfur dioxide	48, 64
2	7.9	benzenemethanimine	77, 105
3	8.4	aniline	66, 93
4	9.7	N-methyl aniline	77, 106, 107
5	9.8	N-methyl aniline	77, 106, 107
6	10.0	N,N-dimethyl aniline	77, 104, 120, 121
7	10.5	N-ethyl aniline	77, 106, 121
8	11.2	naphthalene	102, 128
9	11.6	N,N-diethyl aniline	106, 134, 149
10	12.2	N-phenyl pyrrole	115, 143
11	12.4	indole	89, 90, 117
12	12.6	N-methyl quinoline	115, 128, 143
13	12.7	N-butyl aniline	77, 106, 149
14	15.6	diphenylamine	168, 169
15	16.5	N-methyl-N-phenyl aniline	167, 183

Four felt-tip pens contain triarylmethane dyes such as *light green SF yellowish* (P1 and P2), *crystal violet* (P14) and *water blue* (P16) (Fig. 1). The Py-GC/MS analyses performed at a pyrolysis temperature of 600°C show the presence of several pyrolysis products (3, 8, 10-12) which are in common for all three subclasses (Table 1). In addition, for each of these subclasses specific compounds could be detected.

Light green SF yellowish (C.I. 42095)

As a first step desulfonation seems to take place producing sulfur dioxide (1) [3]. Moreover, the pyrolysis products such as benzenemethanimine (2), N-ethyl aniline (7), N,N-diethyl aniline (9) and N-butyl aniline (13) may be considered specific for this subclass (Fig. 2).

Water blue (C.I. 42755)

The pyrolysis of the dye molecule produces characteristic products identified as diphenylamine (14) and N-methyl-N-phenyl aniline (15) next to sulfur dioxide (1) and N-methyl aniline (4, 5).

Crystal violet (C.I. 42555)

The pyrogram of the ink containing crystal violet dye shows various characteristic pyrolysis products, already identified by Ghelardi *et al.* [2], *i.e.,* aniline (3), N-methyl aniline (4, 5) and N,N-dimethyl aniline (6), whilst molecules with a higher molecular weight were not detected.

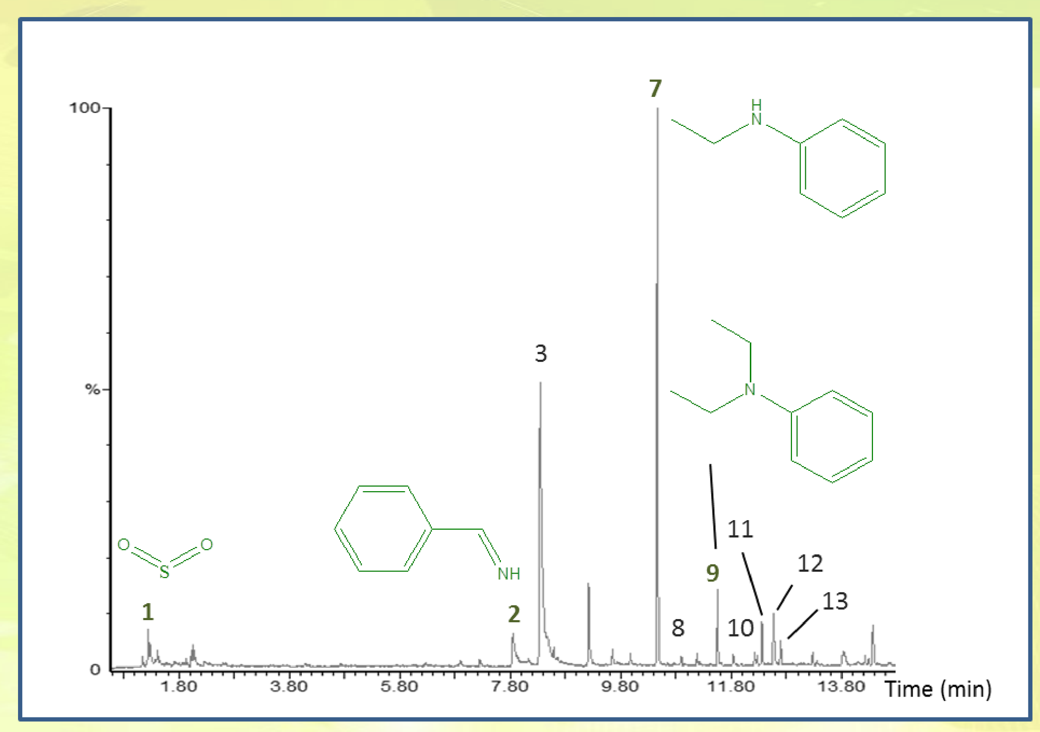


Fig. 2 Pyrogram of P1 containing light green SF yellowish dye

Xanthene dyes

Fluorescein (C.I. 45350) and *eosin Y (C.I. 45380)* belonging to the xanthene class were found respectively in the yellow (P7) and pink felt-tip pens (P8, P9 and P12). In all samples containing xanthene dyes, at a pyrolysis temperature of 600°C, various pyrolysis products were identified: 1,4-dioxane (1), phenol (3), biphenyl (4) and 9-H-fluoren-9-one (8). These have been detected by Ghelardi *et al.* [2] for eosin Y at 550°C.

When increasing the pyrolysis temperature up to 700°C various polycyclic aromatic hydrocarbons could be found (5 - 9) (Table 2). Among these xanthene may be considered highly diagnostic for this class of dyes. Moreover, the production of bromobenzene allows to identify eosin Y.

Tab.2 Main pyrolysis products identified for eosin Y (T_{Py} 700°C)

N.	RT (min)	Compounds	main *m/z*
1	2.9	1,4-dioxane	58, 88
2	7.6	bromobenzene	77, 156
3	8.3	phenol	66, 94
4	13.2	biphenyl	153, 154
5	15.3	phenalene	82, 165
6	15.4	fluorene	165, 166
7	15.8	xanthene	181, 182
8	16.5	9-H-fluoren-9-one	152, 180
9	16.6	phenantrene	178

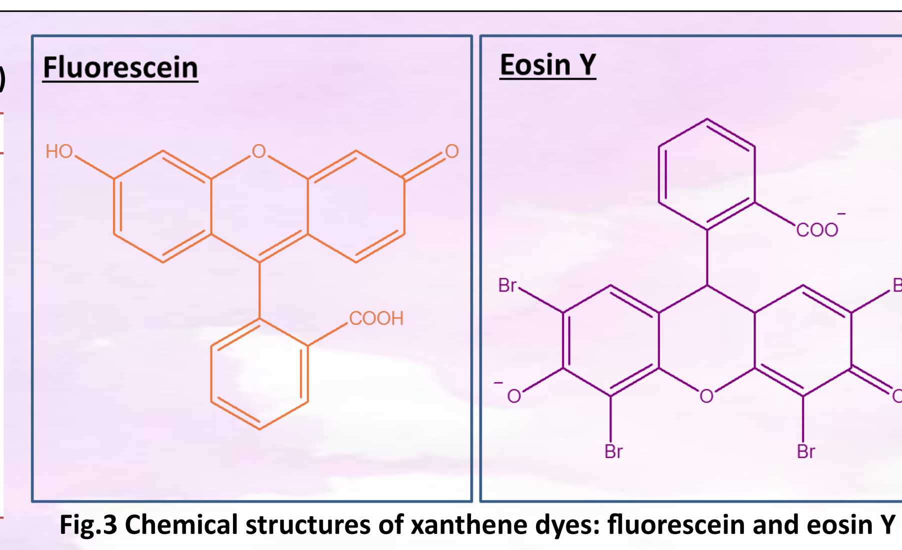


Fig.3 Chemical structures of xanthene dyes: fluorescein and eosin Y

Indigoide dyes

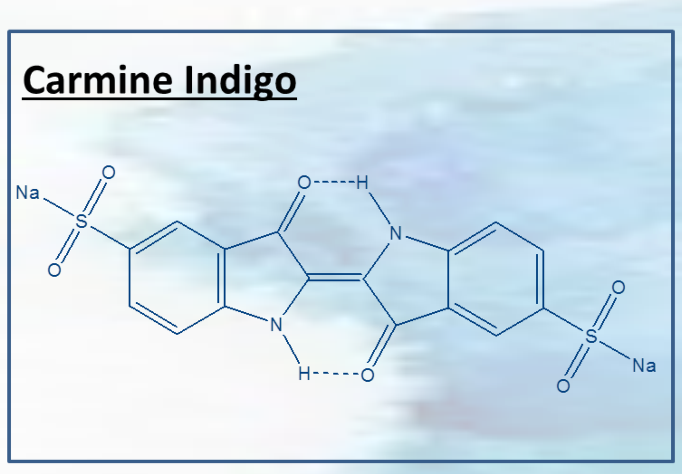


Fig. 4 Chemical structure of carmine indigo

The presence of *Indigo carmine (C.I. 73015)* was assessed in three felt-tip pens (P10, P11 and P13). At high retention times some compounds that could be due to the fragmentation of indigoide molecules were observed: N-ethyl-N-phenyl formamide (2), 3-methoxy-4,7-dimethyl-1-H-isoindole (3), 1,2,3-trimethyl-1-H-indole (4) and 1-methyl-3-acetylindole (5) (Table 3). Moreover, the presence of sulfur dioxide (1) seems to confirm the presence of sulfonated groups which are specific of this type of indigo.

Tab. 3 Main pyrolysis products identified for the indigo carmine dye

N.	RT (min)	Compounds	main *m/z*
1	1.2	sulfur dioxide	48, 64
2	11.6	N,ethyl-N,phenyl formamide	77, 106, 134, 149
3	13.6	3-methoxy-4,7-dimethyl-1-H-isoindole	117, 132, 160, 175
4	14.8	1,2,3-trimethyl-1-H-indole	115, 128, 143, 158
5	15.2	1-methyl-3-acetylindole	158, 173

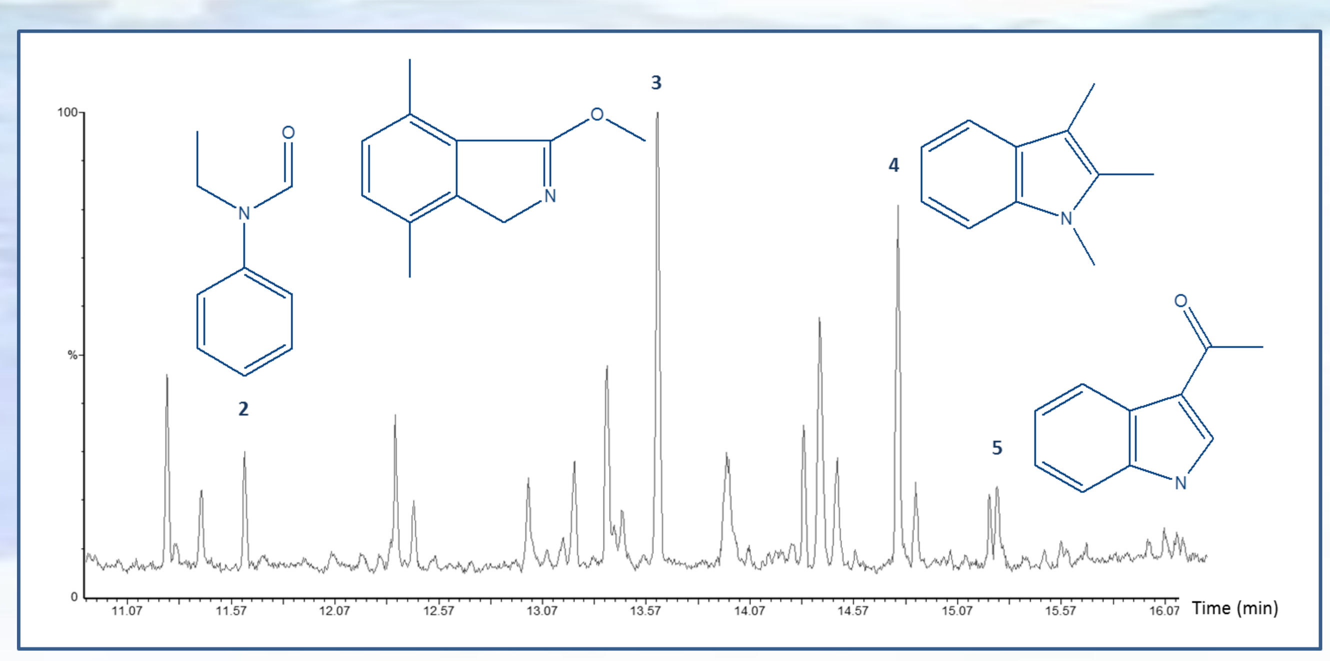


Fig. 5 Pyrogram of P13 containing carmine indigo dye

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