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Modern inks: investigation of felt-tip pens

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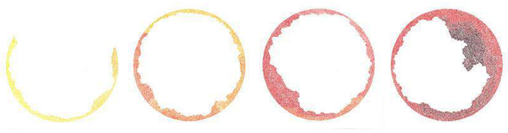
Anne-Flore Cabanis



Inks of felt-tip pens are used by modern artists for the realization of sketches, drawings, copies, architectural drawings and other technical designs. However, these 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 storage conditions. So far, few studies have been addressed to the chemical characterisation of these materials [1] and often information on binders, fillers, dyes and pigments is lacking. In this study felt tip pens (Faber-Castell) used by the French modern artist Anne-Flore Cabanis and other artist pens (Stabilo) were investigated by using an integrated analytical approach. The inks have been analysed with Fourier transform infrared (FT-IR), μ-Raman and visible reflectance spectroscopy, and pyrolysis - gas chromatography - mass spectrometry (Py-GC-MS).

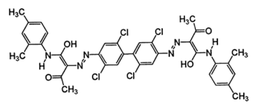
Investigated felt tip pens used by Anne-Flore Cabanis

Anne-Flore Cabanis

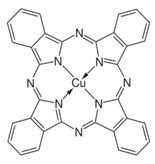
Example of architectural sketch realised with Stabilo pens

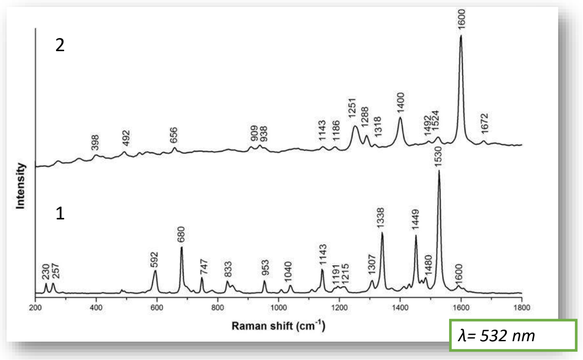
Investigated felt tip pens of 69 Series of Stabilo

PY81 diarylide



PB15:3 phthalocyanine



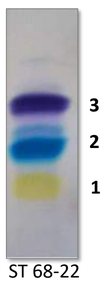


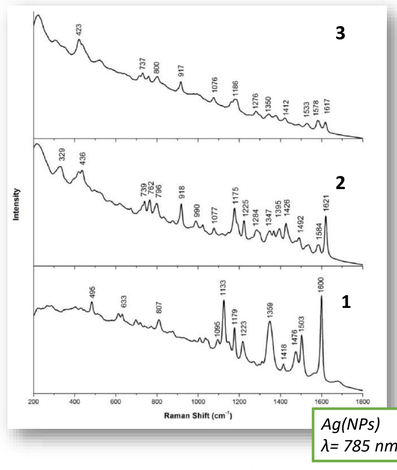
Chloroform

In the Raman spectra acquired on TLC spots phthalocyanine, dioxazine and azo pigments are identified.

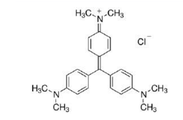
TLC
Raman spectroscopy
SERS

nBuOH:EtOH:NH₃

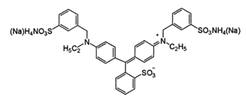




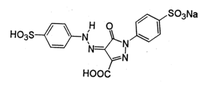
Basic Violet 3



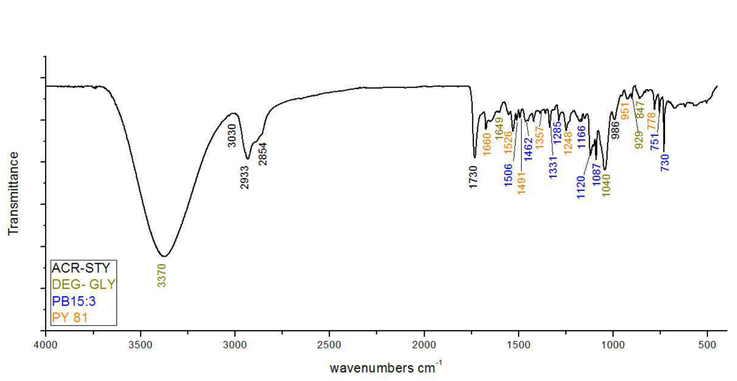
Acid Blue 9



Acid Yellow 23

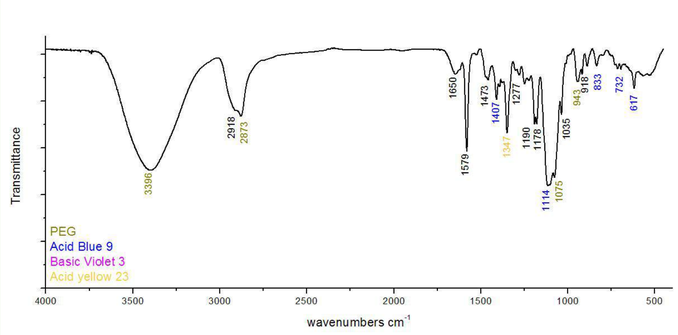


The Stabilo inks contain mixtures of dyes as evidenced by thin layer chromatography (TLC). Surface-enhanced Raman spectroscopy on the TLC spots allowed to identify azo and triarylmethane dyes [2], and rhodamine B.



The FTIR spectra of the Faber-Castell inks clearly show the presence of acrylic-styrene (ACR-STY) binder together with glycerol (GLY) and diethylene glycol (DEG) as solvents. Most intense peaks can be ascribed to pigments. The FTIR spectrum shows the presence of blue phthalocyanine PB15:3 with the diarylide PY81 pigment.

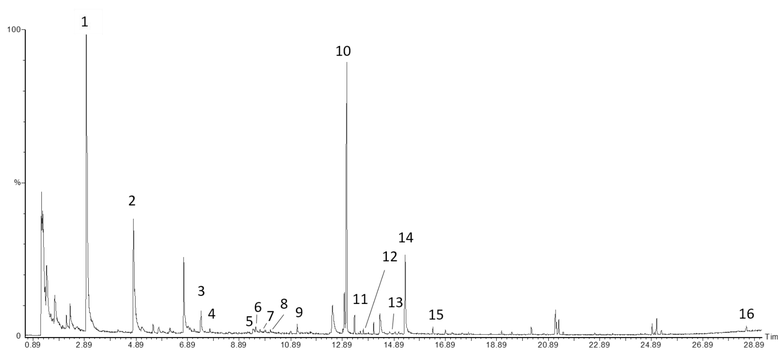
FTIR spectroscopy



In all FTIR spectra of the Stabilo inks the most intense peaks are due to the dyes and to polyethylene glycol (PEG) added as solvent. In these formulations the amount of the binder is generally very low as shown in Recipe 2 [3]. Some peaks are simultaneously due to Acid Blue 9, Basic Violet 3 and Acid Yellow 23 therefore the unique attribution is impossible.

Recipe 2.	Typical dyestuff ink for fibre tip pens
Parts	Component
1.5-3.5	Dyestuff
70-80	Distilled or deionised water
30-20	Diethylene glycol or propylene glycol
0-0.1	Nonionic wetting agent
0-0.1	Resin

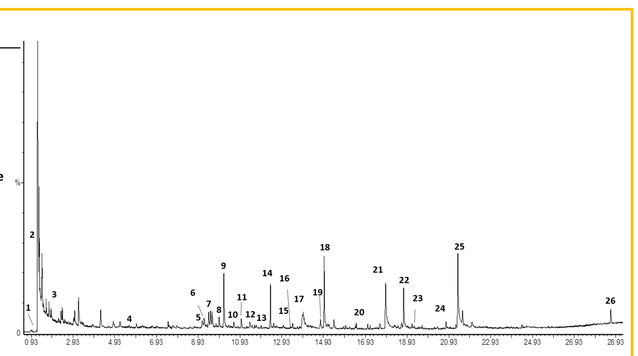
PY-GC-MS



ID	Products
1	Methyl methacrylate
2	Cyclopentanone
3	Styrene
4	Ethylene glycol butyl ether
5	Benzonitrile
6	Phenol
7	α-Methyl styrene
8	Diglycerol
9	Diethylene glycol diethyl ether
10	1-Isocyanato-3,5-dimethyl-benzene
11	2,4,6-Trimethyl-phenol
12	Ethylene glycol monovinyl ether
13	ε-Caprolactam
14	1,2-Benzene dicarbonitrile
15	2,4-Dimethyl aniline
16	Diisooctyl phthalate

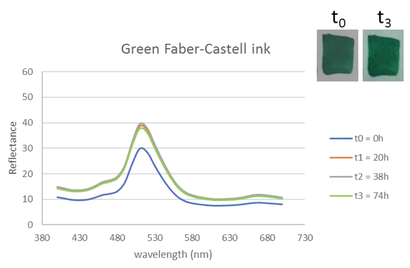
In all pyrograms of the Faber-Castell inks a methyl methacrylate-styrene copolymer binder was identified. The presence of benzonitrile (5) and 1,2 benzenedicarbonitrile (14) suggests the addition of PB15:3; whereas the azo PY81 pigment may be confirmed by the occurence of 1-Isocyanato-3,5-dimethyl-benzene (10) and 2,4-dimethyl aniline (15) [5]. Diethylen glycol (9) and glycerol are used as solvent; phenol and phthalates are added respectively as antioxidant and plasticizer.

ID	Products	ID	Products
1	Chloromethane	14	N-ethyl aniline
2	Sulfur dioxide	15	2,4-dimethylaniline
3	1-Hydroxy-2-propanone	16	Benzothiazole
4	Furancarboxaldehyde	17	N,N-diethyl aniline
5	Benzenthiol	18	Pentaethylene glycol
6	5-Methyl-2-furancarboxaldehyde	19	1,2-Benzenedicarbonitrile
7	Aniline	20	Diphenylmethane
8	2-Methyl-phenol	21	15-crown-5
9	Tetraethylene glycol	22	Heptaethylene glycol
10	N-Methyl aniline	23	Diphenyldisulfide
11	2-Methyl aniline	24	Diphenylamine
12	N,N-Dimethyl aniline	25	Cctaethylene glycol
13	Benzyl nitrile	26	Diisoctyl adipate



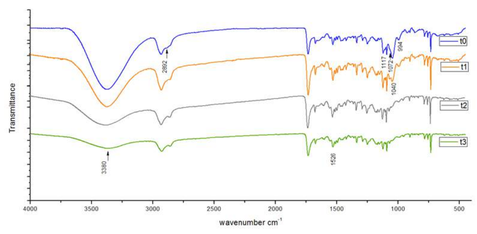
The pyrograms of Stabilo pens show most intense peaks due to the dyes. Triarylmethanes are justified for the presence of N-methylaniline (10) and diphenyl methane (20).The detection of sulfur dioxide (2), benzenthiol (5), N-ethylaniline (14), and N,N-diethyl aniline (16) can be related to **Acid Blue 9** (C.I. 42090); while chloromethane (1), 2,4-dimethyl aniline (15), and N,N-dimethyl aniline (12) point to the occurrence of **Basic Violet 3** (C.I. 42555). Pyrolysis products such as benzyl nitrile (13), benzothiazole (16), 1,2-benzenedicarbonitrile (19), and diphenyldisulfide (h) confirm the addition of **Acid Yellow 23** (C.I. 19140). In these formulations traces of 1-hydroxy-2-propanone (3), furancarboxaldehyde (4) and 5-methyl-furancarboxaldehyde (6) suggest the presence of plant gum as binder [4]. Polyethylene glycol (pyrolysis products: 9, 18, 21, 22 and 25) has been added as a solvent and phenol (8) as antioxidant.

SPECTROPHOTOMETRIC ANALYSES



The reflectance spectra after ageing show a slight increase of the reflectance percentage in the visible range due to colour desaturation.

FTIR SPECTROSCOPY

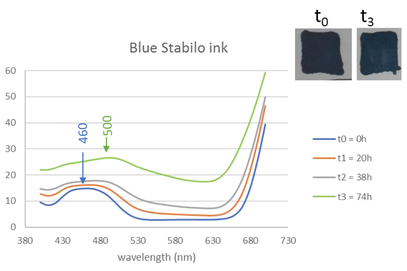


FTIR spectra acquired before and after different exposure times show some differences mainly due to the evaporation of the solvents confirming that pigment lightfastness and the type of binder show relatively high photo-stability. The bands at 3370 cm^{-1} (GLY-DEG), at 1040 cm^{-1} (GLY), at 994 and 847 cm^{-1} (DEG) had noticeably decreased in intensity after 38h of exposure; at the same time, the absorptions due to the PB 15:3 (1120 and 1087 cm^{-1}) became more clearly evident. The absorptions related to pigments and binders seem to be stable under these aging conditions.

AGEING OF INKS

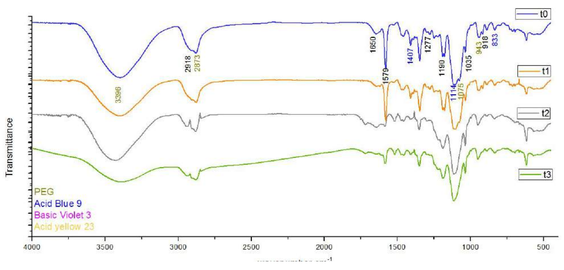
Samples were exposed to an OSRAM Ultra-Vitalux® solar lamp (300W, 230 V) at 10000 lx. The wavelengths of the emitted light were from 280 to 2000 nm. Analyses were performed at different exposure times (t_0=0h, t_1=20h, t_2=38h, t_3=74h).

SPECTROPHOTOMETRIC ANALYSES



The reflectance spectra after ageing show an increase of the reflectance percentage due to the loss of colour. Moreover, the maximun of the reflectance at 460 nm tends to shift towards green tones (500 nm) already after 38 h of the exposure.

FTIR SPECTROSCOPY



FTIR spectra of Stabilo inks after aging show the reduction of peaks attributed to PEG (3396, 2873, 1075 and 943 cm^{-1}). Absorptions at 1650, 1579, 1277, 1190, 1035 and 918 cm^{-1} ascribed to triarylmethanes (Acid Blue 9 and Basic Violet 3) and at 1407 and 1114 cm^{-1} uniquely due to Acid Blue 9, reduce noticeably their intensities over time. Acid yellow 23 (1347 cm^{-1}) instead, shows higher resistance to photodegradation.

References

[1] F. C. Izzo, *et al.* Microchem. J. (2016) 124, 919–928; [2] B. Doherty *et al.* Spectrochim Acta A Mol Biomol Spectrosc (2014) 121, 292–305; [3] G. Pfingstag, JSDC (1993) 109, 188-192; [4] O. Chiantore *et al.*, Int. J. Mass Spect. (2009) 284, 35–41

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