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A STUDY OF GERMAN PRINTING INKS FROM THE EARLY 20th CENTURY

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Abstract

Various coulorful printing inks were developed and widely distributed during the 19th and 20th centuries. However, in comparison to artists' paints from that period, printing inks are not studied in depth. This paper provides a first insight into materials in common German printing inks used at the time to understand the artists' opportunities, predict properties such as light fastness and possible colour alterations. The study is based on literature research and the analysis of two printing ink sample books from the 1920s and 1930s. Complementary analytical techniques were employed to characterise the ink samples, namely Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, Gas Chromatography-Mass Spectrometry (GC-MS) and Scanning Electron Microscopy-energy dispersive X-ray spectroscopy (SEM-EDS). Twenty modern synthetic organic pigments (SOPs) and several traditional pigments as well as metallic pigments were identified in the catalogues. Linseed oil, semi-drying oils and resins (such as Copal and Dammar) were used as binding media. The results will aid decision-making in preservation and conservation of printed works.

***Keywords**: Raman; FTIR; SEM-EDS; GC/MS; Printing Inks; German colour manufacturer; Synthetic organic pigments; Modern Art*

Introduction

Colour prints became a very important communication medium in the 19th century. Although coloured prints are known since the Middle Ages [1] and Fertel already describes coloured inks in 1723 [2], the production of colour prints as a common everyday medium arose only with the invention of fast printing presses, for example the steam-powered rotary printing press, in the 19th century. Accordingly, better printing techniques and reliable printing ink formulations were established to keep up with fast production. The cheaper lithography process was also an important development. However, new printing ink formulations include synthetic organic pigments, which can fade, and sometimes experimental formulations, which were not well designed for long-lasting prints. Studies in the history of inks and their properties are published for example by Ad Stijnman [3, 4]. However, no comprehensive analytical study of modern printing inks together with chemical results in the context of heritage science is known to the authors. To understand the variety and possible problems with prints from that time, especially with the newly developed inks from the early 20th century, this study examines two catalogues of German print manufactures from the 1920s and 1930s: *Gebrüder Schmidt* and *Gebrüder Hartmann*. For the examination, a multi-analytical approach was taken to identify the pigments, extenders and binding media of the printing inks.

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Historical context – printing inks and artists printing practice around 1900

Printing was a common technique used by artists around 1900. Signac, Kirchner, Kollwitz, Schmidt-Rotluff, Munch and others have produced regulary woodcut prints and etchings. They were part of a revival of traditional, but in terms of technology outdated, printing techniques used mostly by artists and artist book publishers as well as for packaging material and cheaper advertisement. Artists printing at that time was far from the common fine printing manufacture around 1900, which was mostly done by lithography [5]. Printing was conducted in large printing studios. Paris was the centre of art printing in the Western culture in the 19th century. Newspaper prints, advertising poster prints or books were produced in large scales. An example is the *Imprimerie Chaix* (1845 - 1965) in Paris, which focused on Belle Époque posters and art publishing with a monthly subscription system (*Les Maîtres de l'Affiche*) [6]. Many printmakers, which were specialised in traditional etching techniques and woodcut, closed their studios in the beginning of the 20th century. The traditional studios, which were still printing after the Second World War, were mainly printing artists' prints, not commercial books or advertisement anymore due to the higher prices of the slower techniques.

The rapid processes had a steep rise from the 1830s onwards due to the invention of faster presses. For example, new technologies to apply the ink onto the machine improved the speed of the printing process. These fast processes required finer and larger quantities of printing ink than the hand-printed editions beforehand. Coloured printing inks (with mineral pigments) were problematic for printing machines. Therefore, with the help of the chemical industry, new synthetic pigments were introduced in printing ink formulations. Furthermore, various specially modified printing inks for different printing methods and production speeds were developed. The Lefranc printing ink factory, for example, had its own research laboratory for new formulations [7]. Different mills were used for different formulations: The three-roll ink mill was the common mill for fine black inks, often with a watercooling system. Coloured pigments were usually ground on a stone mill, which is not as fine and therefore better for traditional mineral pigments and other coarse pigments.

Artists often used traditional techniques, but we assume that they applied manufactured printing inks as well, especially for colours, as the production of fine ink is quite labor-intensive and ready-made inks were available. The inks need to have other qualities than artists' paints; hence, these would not work as substitutes. Many artists worked usually together with professional printers; for example, Munch worked with Sabo, Angerer, Nielsen, Clot, Lemercier and Lassally [8], Géricault worked with Motte and Hullmandel and Toulouse-Lautrec with Clot. The well-known printer Roger Lacourière worked together with Picasso, Braque, Chagall, Masson and Miro [9].

However, printing inks at the turn of the 19th to the 20th century are understudied. Certainly, printing inks were also mixed by printers or artists, as some manuals from the time suggest [10]. There was a vivid exchange between printmakers, knowing their craft, and artists, experimenting with different techniques. The gallerists after 1930 even encouraged their artists to print for example their exhibition advertisements or a variation of their paintings as prints were easy to produce in editions, which were sold to collectors [9]. A printmaker, who is known to have produced many advertisement posters for exhibitions with artists, was Mourlot. Artist illustrations, books and print albums is a field, which needs closer investigations starting from French artists such as Delacoix (Faust 1828) to printmakers such as Lucien Pissarro and German Expressionists [11, 12].

Contemporary publications

Authors of artists' and printers' manuals from that time only sometimes discuss printing inks in detail [10]. More often, these manuals list necessary raw materials and describe their origin [13, 14]. The books, covering detailed recipes for printing inks, are usually intended for paint manufacturers or have an encyclopedic approach, summarizing the knowledge of the time [7, 15]. Some of them are certainly manuals for artists who have joined the etching revival of historic printing techniques such as etching and woodcut prints, as a counter-development answering the industrialisation of printmaking [10, 14]. However, some books only cover the etching process, not discussing the printing process at all; hence, no information about the printing inks is given [16].

In general, the production of printing inks discussed in the contemporary literature can be summarised by these steps: first, the production of the binder and colourants (soot or colour pigments), followed by mixing these, for example in a three-roll mill. Hereby very good quality binder is used. Best is linseed oil, which is cooked slowly in several steps up to 380°C, for up to 12 hours. This produces a strong heat-bodied binder with good drying properties. Soyabean oil is mentioned as well [17]. Composition binders were used quite frequently for cheaper printing inks, for example for newspapers. They can include petroleum oil, shale oil or resin oil mixed with rosin and siccatives (metal soaps). Bottler describes a binding medium for book-printing inks in his book about lacquer and varnish production (1924) [15]. He gives details of the parts (by weight) for three different formulations whereas only the part of the oil is reduced (from 13 to 8.7 parts); more oil is added for “weak” varnishes, less oil for “stronger“ varnishes. The following compounds are listed (parts in brackets): linseed oil (13, 10.5 or 8.7), resin oil (distillates of colophony obtained using temperatures around 300°C) (24 parts), colophony (21 parts), thick turpentine (0.5 parts), resin soap (0.5 parts).

Printing inks and their properties are very different from paints, which are usually applied with a brush, because printing inks need to function in a sophisticated, mechanical process onto paper. The formulation of the printing inks is dependent on the intended printing technique (mezzotint, engraving etc.). Desired ink properties are listed usually like this: very homogeneous, not sticky, viscous, high binding strengths for pigments, good drying properties, not striking through the paper and not rubbing off. The ink has to transfer easily to the paper. It should not be sticky as any surplus on the printing plate should be easily removable. These requirements are not easy to achieve and frequent difficulties are mentioned [17-25]. These include problems occurring during the printing process such as working away from the ink rollers, lack of distribution, drying on the rollers, offsetting, flooding the type, picking up, filling the forms, tinting the forms, or after the printing process such as rubbing off after drying, graining on the roller, drying too fast or not drying fast enough. Pigments, which are listed in contemporary publications about printing inks, include mineral pigments and traditional synthetic pigments: lead white, lithopone, zinc white, Titanium white, minium, cadmium yellow, chrome yellow, ultramarine blue, vermillion, Prussian blue, chrome green and silk green (Prussian blue & chrome yellow). They are used for rough inks. Frequently described in these publications are organic dyes, synthetic organic pigments, madder and coal tar dyes as well, as these pigments are usually very fine and therefore very suitable for printing inks.

Experimental part

Materials

The *Stiftung Preußischer Kulturbesitz* holds a collection of printing inks catalogues. They were produced by their manufacturers and have served as advertising material. These books often include a description of the history of the company and several images, printed in different techniques, to show not only the colours but also other qualities of the inks for the different printing processes. These include, amongst others, transparency or opacity, flexibility and ability to stick to smooth or special paper.

For this study, two catalogues have been selected to investigate pigments, extenders and binding media for printing inks from the 1920/30s. They are by *Gebrüder Schmidt* and *Gebrüder Hartmann* (Fig. 1).

Fig. 1. Examined case studies, *left:* Sample book of Gebrüder Schmidt printing inks [20], *right:* Book '*Vom Drucken und von Druckfarben'* by Gebrüder Hartmann (1931) [25]

Gebrüder Schmidt were actively involved in the printing world over several decades, which can be traced by their advertisements in many newspapers in various years. Apart from advertisement, they have printed books with fine illustrations to show the quality of their printing inks (Fig. 1 left, Fig. 2 and Fig. 3).

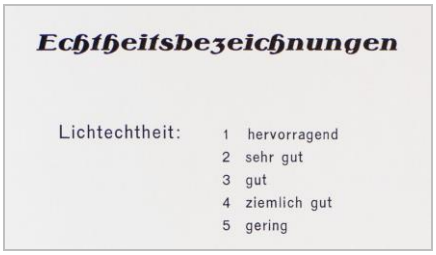
Fig. 2. First pages of printing ink catalogues by Gebrüder Schmidt *left*: 1898 [19], right: 1910 [21]

The *Gebrüder Schmidt GmbH* was founded by the brothers Ernst and Rudolf Schmidt in 1878 in Bockenheim (Frankfurt) [18]. In 1889, they have bought a newspaper printing ink factory in Berlin and in 1907 another factory in Berlin-Heinersdorf. Berlin finally became the headquarter in 1928. *Gebrüder Schmidt* printing inks became very successful and have established factories in ten European countries by the 1930s. Their products were used worldwide and their good printing ink quality earned them, for example, a golden medal at the 1900 Paris Exposition (Fig. 2 right). The printing ink catalogues show prints in different techniques and with various colours [19-21]. Below each print, the used inks with names and numbers are mentioned, for example red no. 1009, yellow no. 2013 etc. (Fig. 3).

The analysed catalogue [20] was printed between 1914 and the Second World War, based on the inscription "*Berlin-Heinersdorf*" on the cover of the catalogue (Fig. 1 left) and the font of "*Echtheitsbezeichnungen*" on the first page (Fig. 4). This font is called *Fette Bravour-Kursiv* and has been introduced in 1914 [22]. The catalogue has 22 colour plates containing nine colours each (198 colour patches in total). The initial study was focused on 120 colour patches suggesting synthetic organic pigments, based on colour and name.

Gebrüder Hartmann were producing printing inks from 1905 onwards in Halle-Ammendorf, Germany [23]. The company has published a number of educational books, which promote their inks and provide application notes to users. *Gebrüder Hartmann's* book about food printing inks shows for example an illustration about what happened when wrapping for butter is printed with unsuitable ink: the ink will stick to the butter [24]. The examined book in this study is called '*Vom Drucken und von Druckfarben',* (engl. 'about printing and printing inks') [25] and is dated to 1931 (Fig. 1). It contains twenty plates showing different inks. Underneath each plate are the names of the printing inks used for the print (Fig. 5).

Fig. 3. Print examples with notes on used printing inks in *Gebrüder Schmidt* catalogue from 1910 [21]
left: Ballon with *Bronceblau No. 3021*, *right:* "O. Ligner: Carmen" (detail with ink no. enlarged)


Echtheitsbezeichnungen

Lichtechtheit:
1 hervorragend
2 sehr gut
3 gut
4 ziemlich gut
5 gering

Fig. 4. *Echtheitsbezeichnungen* in ink sample book by Gebrüder Schmidt [20]

Fig. 5. Three *Gebrüder Hartmann* inks for packages (incl. *Federfarbe 000, Hallenserrot 114 and Concentrablau 334*), [25] p. b107

They have also printed on various challenging papers for inks due to different paper colours, surfaces and thicknesses. The book starts with a very short introduction about the history of printing inks and general printing ink formulations, including the description of traditional pigments used for printing inks. Coal tar pigments are mentioned but are not further described. Different printing techniques are also explained. The book focuses in the main part on the usage of printing inks and the various additives and modifiers. The ingredients of the printing inks are mentioned only in very general terms (e.g., “linseed oil”,” copal” and “dammar”) but no formulations are given. This book is a very good example of early application notes of special modified inks and additives and their correct use. The additives have names such as “*Schnelltrockner Quick No. 1606, Offsettinktur Nr. 1740*” or “*Trockenstoff Quick Rapid Nr. 1612*”. This provides general properties and usage (e.g., siccative), but does not provide formulations in contrast to earlier publications such as the book by Bottler from 1924 [15], which is written for ink manufacturers, not users, i.e., printmakers.

Analytical Methods

A multi-analytical approach was followed to analyse the inks in the two catalogues. Microscopy techniques, energy dispersive X-ray fluorescence spectrometry, Raman spectroscopy, Fourier transform infrared spectroscopy, and gas chromatography-mass spectrometry were used to identify binding media, organic and inorganic pigments and fillers.

The print examples and colour charts in the books were visually examined using a Zeiss Stereo Discovery.V8 microscope with 8:1 manual zoom range.

Raman spectra were acquired with a *Horiba Scientific* µ-Raman spectrometer with *Xplora* Raman microscope equipped with a laser operating at 785nm. The analysis was carried out directly on the catalogues. The laser beam was focused with 20, 50 or 100x objective lens, laser intensity varying from 1.0 to 100%, depending on the analysis. Raman radiation was dispersed with 1200lines/mm or 1800lines/mm grating. Average spectra from 5 to 20 measurements (20 to 60 seconds measuring time) were collected in variable ranges from 100 to 2500cm^{-1}. The background (paper and priming) was subtracted from the obtained spectra, and the result compared with the spectra in the *Rathgen-Forschungslabor* reference library and the SOPRANO library (KIK-IRPA).

Infrared spectra were collected on tiny samples taken from the patches with a Paragon 1000 PC Infrared Spectrometer, fitted with a FT-IR microscope (Perkin Elmer) in transmission mode in the range between 4000 - 600cm^{-1}, with a resolution of 4cm^{-1}. Samples were mounted on a diamond cell (High Pressure Diamond Optics). The resulting spectra were compared with reference spectra from *IRUG* and *Sadtler* databases as well as references from the *Rathgen-Forschungslabor*.

Scanning electron microscope Quanta 200 from FEI coupled with an energy dispersive X-ray fluorescence spectrometer (XFlash 4010 from Bruker) was used for microscopy images and elemental analysis. Results were obtained at 15 or 20kV.

Binding media analysis was carried out with an Agilent gas chromatograph (GC 7890B) coupled with a mass spectrometer (MSD 5977A). For analyses, the samples were dissolved in methanol and a part was derivatised with MethPrepII (0.2mol/L solution of m-trifluoromethylphenyl trimethylammonium hydroxide in methanol) for 5 hours at 60°C. The extracts were analysed with a binding media standard method (injection of 1.0μL, 1.2mL/min Helium, DB-5MS-column, ramp: 80ºC (3 min isotherm), 10ºC/min to 200ºC (3 min isotherm), 20°C/min to 300°C (30 min isotherm), Interface GC/MS: 300ºC, MS fragmentation at 70eV, ion source at 200°C, in scan mode from 9.5 min 40-600 amu). The results were compared to the NIST database and the *Rathgen-Forschungslabor* reference library.

Results and discussion

A summary of the analytical results of the two examined catalogues by *Gebrüder Schmidt* and *Gebrüder Hartmann* are presented in Tables 1 and 2, respectively.

Table 1. Identified pigments and extenders in the *Gebrüder Schmidt* catalogue [20]

Name	Pigment / Extender	Class	Identified in the following *Gebr. Schmidt* inks
Pigment Blue 62 / Brilliant Blue	PB62	SOP, Triaryl Carbonium	Brillantechtgrün 453
Pigment green 1 / Brilliant green	PG1	SOP, Triaryl Carbonium	Brillantechtgrün 453
Hansa Yellow G	PY1	SOP, Arylide Yellow	Echtgelblack 254*
Hansa Yellow GR	PY2	SOP, Arylide Yellow	Echtgelblack 255*
Hansa Yellow 10G	PY3	SOP, Arylide Yellow	Echtgelblack 248*, Echtgelblack 250*, Brillantechtgrün 456, Echtgrünlack 462
Arylide Yellow GX	PY73	SOP, Arylide Yellow	
Hansa Orange RN	PO5	SOP, Beta-Naphthol	Echtorangelack 260* Zinnoberersatz 147
Toluidine Red	PR3	SOP, Beta-Naphthol	Kalenderrot 1047, Echtrot 1205, Zinnoberersatz 145, Universalrot 1038
Permanent Red R	PR4	SOP, Beta-Naphthol	Echtrot 1200, Rotlack 138
Permanent Red F4R	PR8	SOP, Naphthol AS	Echtrot 1213
Permanent Bordeaux TRR	PR12	SOP, Naphthol AS	Flammrot bläul. 1207
Barium Lithol Red	PR49:1	SOP, Metallized Azo	Spezialrot 199, Brillantrot 159, Kaiserrot 1026
Pigment Lake RedC	PR53:1	SOP, Metallized Azo	Leuchtrot 1016, Victoriarot 1050, Brillantrot 142, Flammrot 1201, Brillantrot 156, Zinnoberersatz 1202, Excelsiorrot 1042, Kaiserrot 1025, Spezialrot 198, Geraniumlack 175
Pigment Red 54	PR54	SOP, Metallized Azo	Brillantbordeaux 1209, Florentinerlack 165
Lithol Rubine	PR57:1	SOP, Metallized Azo	Violett 628
Permanent Rose	PR60	SOP, Metallized Azo	Anticarmin 109, Magentalack 1018, Purpurinlack 196

Name	Pigment / Extender	Class	Identified in the following *Gebr. Schmidt* inks
Rhodamine 6G	PR81	SOP, Triaryl Carbonium	Brillantechtrosa 1211
Alizarin Crimson	PR83	SOP, Anthraquinone	Krappcarmin 132
Minium, Red Lead	PR105	Mineral pigments	Zinnoberersatz 1202
Pigment Violet 2 / Purple	PV2	SOP, Triaryl Carbonium	Violettlack 642
Pigment Violet 27 Permanent Violet	PV27	SOP, Triaryl Carbonium	Echtviolett 648
Prussian blue	PB27	Modern synthetic pigment	Krappcarmin 132, Echtgrünlack 462, Granatlack 182
Baryte	PW22	Extenders	Underneath all patches, used as priming
Gypsum	PW25	Extenders	Underneath all patches, used as addition in the priming
Carbon-based black	(PBk6)	Carbon-based black	In grey frame surrounding the colour patches

Table 2. Identified pigments and extenders in the *Gebrüder Hartmann* catalogue [25]

Name	Colurant/ Extender	Class	Identified in the following *Gebr. Hartmann* inks (page, sample no.):
Aluminium flakes		Metal flake	*Silberdruckfarbe* 673 (p. b81, DF-07)
Pigment Red 53:1	PR53:1	SOP, Metallized Azo	*Hallenserrot* 166 (p. b17, DF-06), *Hallenserrot* 114 (p. b107, DF-10)
Barium Lithol Red	PR49:1	SOP, Metallized Azo	*Normalrot* 27456 (p. b55, DF-04)
Permanent Red R	PR4	SOP, Beta-Naphthol	*Plakatrot* 9001 (p. b87, DF-08)
Vermillion	PR 106	Mineral pigment	*Deckrot* 4505 (p. b77, DF-05)
Red perylene pigment (?)		SOP	*Bathychrom-Rot* 25764 (p. b191, DF-13)
Magenta (basic violet 14) (?)	BV 14	dye	*Prachtblau* 326 (p. b11, DF-01)
Prussian blue	PB27	Synthetic pigment	*Bathychrom-Blau* 25765 (p. b191, DF-15), *Deckgrün* 20020 (p. b77, DF-06), *Concentrablau* 334 (p. b107, DF-11), *Bathychrom-Grünschwarz glänzend* 3952a (p. b177, DF-12)
Ultramarine blue	PB29	Mineral pigment	*Prachtblau* 326 (p. b11, DF-01)
Unidentified yellow pigment			*Normalgelb* 882 (p. b55, DF-03)
Hansa Yellow 10G	PY3	SOP, Arylide Yellow	*Deckgrün* 20020 (p. b77, DF-06), *Bathychrom-Gelb* 25763 (p. 191, DF-14)
Baryte / Barium sulfate	PW22	filler	In nearly all examined samples (DF-01, 02, 03, 04, 05, 06, 08, 10, 11, 12)
Kaolinite	PW19	filler	in all analysed *Bathychrom* colours (DF-12, 13, 14, 15), in all blues (DF-01, 11, 15) and some reds incl. *Bathychrom-Rot* 25764 (p. b191, DF-13), DF-03, DF-05 and DF-10, in all examined yellows (DF-03, 14)
Calcite / chalk	PW18	filler	in all analysed *Bathychrom* colours (DF-13, 14, 15), traces in DF-11
Soot, bone black		Carbon-based black	*Kosmosschwarz* (p. b95, DF-09)

Gebrüder Schmidt printing inks

Twenty modern synthetic organic pigments (SOPs) were identified: Five Triaryl carbonium pigments, four Arylide yellow pigments, five metallized Azo dyes and several Naphthol pigments have been used in *Gebrüder Schmidt* printing inks [20]. They are listed in Table 1.

The considerable long list can be explained by the fact that fine pigments, such as SOPs, are necessary for homogeneous inks and the industry has developed new SOPs at the same time as printing became faster and new printing techniques, especially for photo-mechanical-reproduction processes, have been developed. Barium sulfate was also identified in several inks (*Echtgelblack 248, 250, 254, 255, Echtorangelack 260, Krappcarmin 132, Granatlack 182, Echtgrünlack 462, Bismarckbraun 510*). It was used as priming underneath all patches. A weak Raman band also indicates gypsum in the priming. A grey frame is printed on top of the priming surrounding the colour patches (Fig. 6).

Fig. 6. First chart in *Gebr. Schmidt* printing inks book, yellow printing colours [20], see also figure 8

The grey printing ink contains baryte and carbon black. Minium was used as substitute for a vermillion colour as it is called "*Zinnoberersatz*". ("*Zinnober*" means vermillion in German, "*Ersatz*" means substitute).

The distribution of the pigments in the catalogue can be summarized as follows: various SOPs have been identified in 59 of the 120 analysed colour patches. In 37 patches, fluorescence prevented the identification of the components. The remaining 24 patches were coloured using inorganic pigments. PG1 and PV3 were often mixed with Prussian blue to obtain greenish or violet shades of blue (e.g., *Echtgrünlack 462*). The arylide yellow PY1 was found very often, both alone and mixed with Prussian blue to obtain green hues. The arylide yellow pigments PY2, PY3, PY73 were also identified. Concerning the red colour patches, the metal salt azo pigments PR53:1 and PR57:1 was mostly used (Fig. 7). PR53:1 was identified in ten red, pink, purple and violet colour patches. The metal salt azo pigments PR49:1, PR54, PR60 were identified in a few patches (see Table 1). The anthraquinone red PR83 was only identified in one colour patch: *Krappcarmin 132*. In some instances, SOPs were mixed with inorganic pigments and fillers. Rarely, two SOPs were mixed to obtain a specific hue (e.g. *Brillantechtgrün 453*). Many yellow, orange, and red SOPs exist with similar chemical structure and hence show very similar spectra. In consequence, their identification was particularly challenging. Yellow SOPs showed very weak Raman bands in comparison to the other colours. In addition, they have been often mixed with inorganic pigments, such as baryte or Prussian blue.

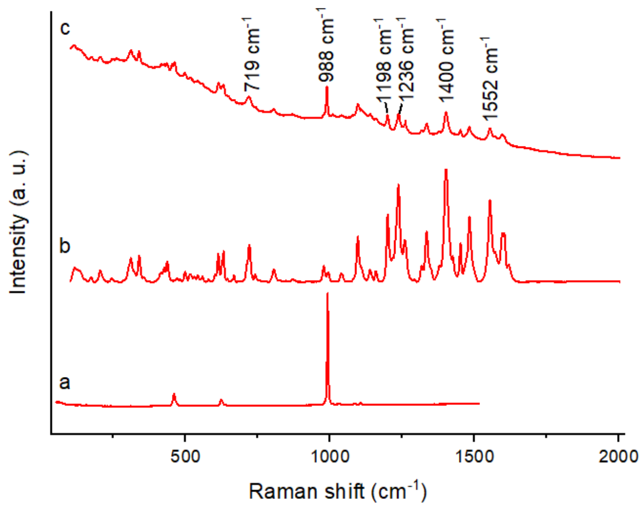


Fig. 7. (a) Raman reference spectrum of baryte, (b) Raman reference spectrum of Pigment Red 57:1 (c) Raman spectrum of the *Gebrüder Schmidt* violet ink named *Violett 637*

To obtain several hues, the inorganic fillers were added in different concentrations (Figs. 6 and 8). The presence of arylide (Hansa) yellows PY1, PY2, PY3 and the orange β-naphthol PO5, has been confirmed using infrared spectroscopy.

Gebrüder Hartmann printing inks

The results of the analysis of selected printing plates in the *Gebrüder Hartmann* catalogue '*Vom Drucken und von Druckfarben*' [25] show barium sulfate in all inks, apart from the metal flake ink *Silberdruckfarbe 673*. Kaolinite was also identified in almost all samples. Calcite however was only present in the so-called *Bathychrom* inks, which are made for three-colour intaglio. The three-colour intaglio sample in the book (between page 190 and 191, therefore labeled here as p. b191) is printed with the *Bathychrom* colours yellow (25763), red (25764) and blue (25765). The adjacent text (p. 192) indicates that the colours shall be slightly transparent for that technique, which explains the kaolinite extender. Prussian blue was found in most blue and green inks, ultramarine blue only in *Prachtblau 326*. The examined green was mixed with Prussian blue and Hansa yellow 10G (PY3). Soot was used in the black ink. The synthetic organic pigment PR53:1 is the colourant in *Hallenserrot 166* (Fig. 9). It is a quite stable and common printing ink pigment. The identified Barium Lithol Red PR49:1 is not as heat stable but common in ink formulations, here only identified in *Normalrot 27456*. PR4 was identified in *Plakatrot 9001*. The analyses show more synthetic organic pigments, which need further investigation with additional and/or modified techniques.

A semi-drying oil is present as the major component in all analysed printing ink samples, based on typical fatty acid distribution in the derivatised samples (Gebr. Hartmann inks DF-11 *Concentrablau 334*, DF-12 *Bathychrom-Grünschwarz glänzend 3952a*, DF-13 *Bathychrom-Rot 25764*, DF-14 *Bathychromgelb 25763*) analysed by GC/MS. The chromatogram of the derivatised sample DF12 (Fig. 10) shows Suberic acid methyl ester (ME) at 13.85min; Azelaic acid ME (15.2min); Hexadecanoic acid ME (20.9min); (Z)-9-Octadecenoic acid ME (23.2min); (E)-9-Octadecenoic ME (23.3min); Stearic acid ME (23.5min); Eicosanoic acid ME (25.7min); Behenic acid ME (27.7min); Lignoceric acid ME (30.0min).

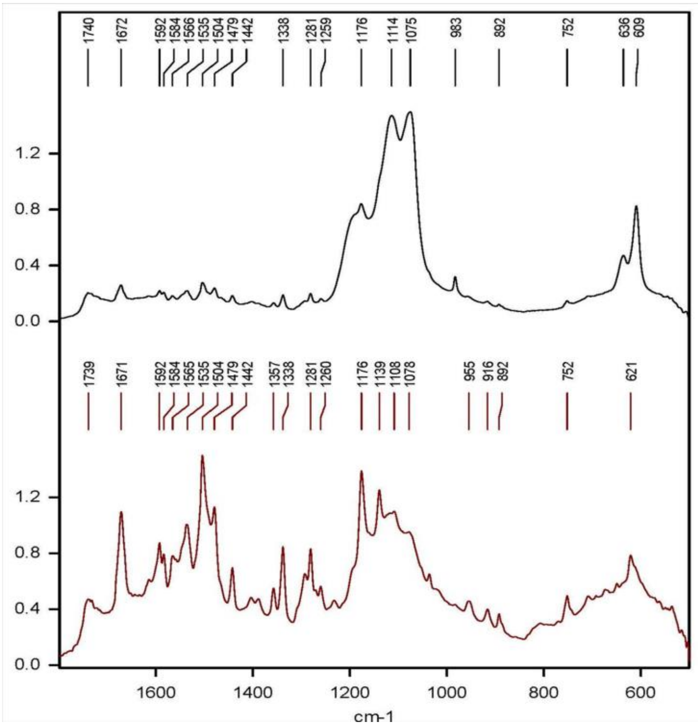


Fig. 8. FTIR spectra of *Gebr. Schmidt* chart 1 plate 1 *Echtgelblack 248* (top) and plate 3 *Echtgelblack 250* (below). Pigment Yellow 3 is the main colouring component in both plates. Plate 1 contains more barium sulfate (see Fig. 6).

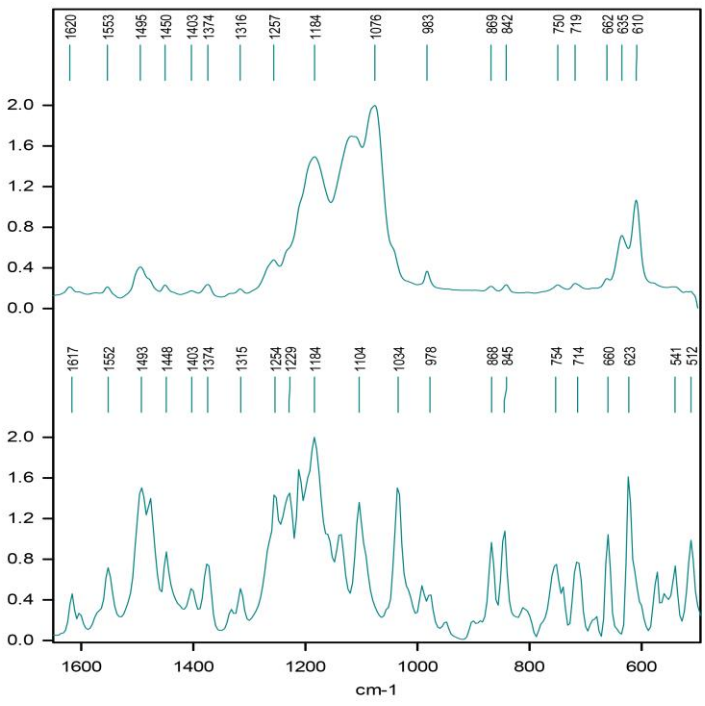


Fig. 9. FTIR spectra of DF-02 *Hallenserrot 166* (top), Reference of Pigment Red 53:1 (below)

Very high Oleic acid ME peaks of the derivatised samples (compared to the Stearic acid ME peaks) and the low Azelaic acid ME peaks indicate low oxidisation of the oil. The high Oleic acid ME, Behenic acid ME and Lignoceric acid ME peaks may indicate the use of a rapeseed oil in the formulation [26]. The high amount of C18-fatty acids might be also due to the metal stearates, which are indicated by the presence of 1585, 1539 and 1455cm^{-1} bands in the FTIR spectra of the samples. This needs to be further investigated by examining more reference materials accompanied by archivals research, e.g., studying recipe books of the company.

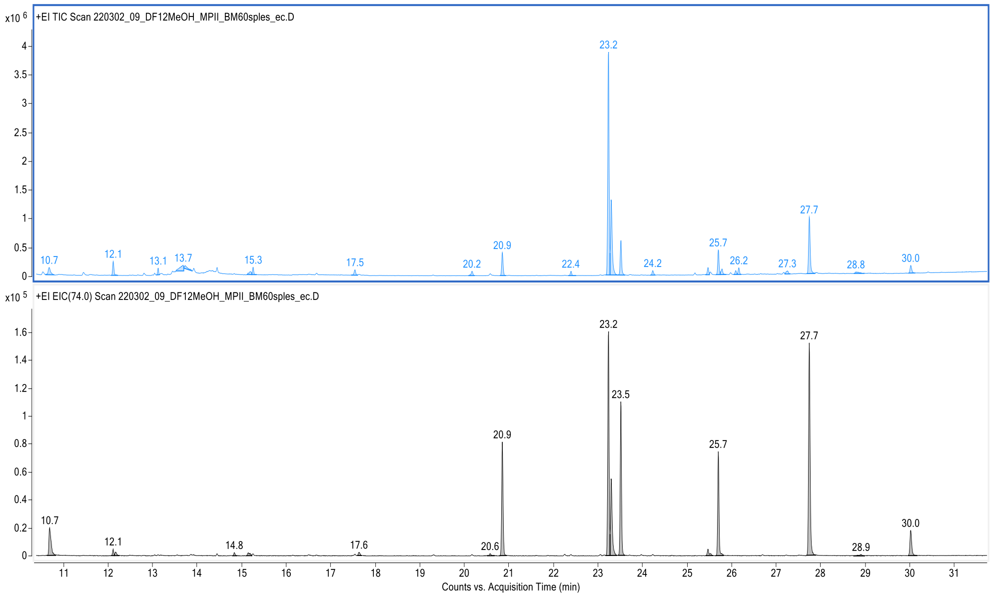


Fig. 10. Chromatogram of derivatised sample DF-12 (*Bathychrom-Grünschwarz glänzend* 3952a), *top:* Total Ion current (TIC), *below*: Extraced Ion Chromatogram (EIC 74.0 m/z).

In addition, diterpene resin was present in very small quantity (identified in DF-11, 12, 13 and 14). Resin markers such as dehydroabietic acid derivatives indicate that (Methyl pimarate (25.18min), Methyl-6-dehydrodehydroabietate (26.1min), Methyl dehydroabietate (26.2min), Methyl-3-Hydroxydehydroabietate (27.3min), Methyl-7-oxodehydroabietate (28.8min).

In publications, deterpene components are usually added to an ink to increase drying time and to change other properties like workability and gloss. However, it needs to be further investigated, whether that small amount could also originate from the paper support.

Conclusions

Printing inks have complex formulations, designed especially for the printing process. They became readily available in the 19th century and several companies specialised in producing fine, modified and improved printing inks in the beginning of the 20th century. Artists often printed their work in large professional printing studios and sometimes in their own workshop.

The two examined printing ink catalogues give an insight in the variety of pigments used, which were developed parallel to the professionalisation and specialisation of ink manufacturing. Several synthetic organic pigments have been identified: PB62, PG1, PY1PY2, PY3, PY73, PO5, PR3, PR4, PR8, PR12, PR49:1, PR53:1, PR54, PR60, PR81, PR83, PV2, and most probably the dye Basic Violet 14. Prussian blue (PB27), ultramarine blue (PB29), red lead (PR105) and vermillion (PR106) as well as carbon-based black and the extenders baryte (PW22), gypsum (PW25), chalk (PW18) and kaolinite (PW19) were used. Inks with aluminum flakes have been available for special effects. This shows the wide range of pigments, which have been mixed to several hues ready to use for printing. Binding media for printing inks are cooked drying oils or semi-drying oils, but also resin components were identified.

Detailed compositions, which are described in some contemporary books, need further investigations. It is necessary to analyse these inks with a multi-analytical approach due to their complexity. This initial study provides a first overview about common printing ink components, used by two German ink manufactures, for conservators, artists and conservation scientists.

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Authors Contributions

Conceptualisation and methodology E.C., investigation and analysis *Gebr. Schmidt* inks A.B. and E.C., investigation and analysis *Gebr. Hartmann* E.C., historical context printing inks E.C., writing - analyses and results E.C. and A.B.

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