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Model compounds of iron gall inks – a Mössbauer study

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Abstract Ferrogallic inks were used for at least two millennia before they became obsolete in the 20th century. The chemistry of such inks is, however, still largely unclear. Today it is of particular interest for the conservation of old manuscripts. ^{57}Fe Mössbauer spectra of the ink on historical documents showed the presence of Fe(II) oxalate and of Fe(III) sites presumably representing iron oxihydroxides. To obtain more information on the behaviour of ink on paper we have performed Mössbauer studies at 300 and 4.2 K on iron gall inks prepared from $FeSO_4 \cdot 7H_2O$ and tannin. These inks were either written on paper or isolated as a precipitate by centrifugation. In the dried precipitate there is still a strong contribution of the $FeSO_4 \cdot 7H_2O$ which is absent in the same ink written on paper, for which a broad ferrous component with a quadrupole splitting (QS) of about 2.5 mm/s was found. The dominant Fe(III) site present in all inks on paper with QS $\approx$ 0.82 mm/s is not Fe(III) gallate and different from the precipitates. We propose that nanoparticulate oxidic clusters or molecular composites covered by a shell of polymerized oxidation products of the phenols are formed on the paper.

Keywords Mössbauer spectroscopy · Ferrogallic ink · Ancient documents · Model compounds

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1 Introduction

Iron gall inks were important writing media for nearly 2000 years [1]. They are made by mixing solutions of ferrous sulfate with extracts from gallnuts, which are rich in tannin, a mixture of different polyphenols (PPH), i.e., aromatic compounds having two or more OH groups attached to their ring systems. Documents written with such inks often suffer from serious degradation processes [2, 3]. Non-destructive analytical methods developed in recent years have led to renewed interest in the investigation of historical documents [3, 4], particularly as the chemical nature of the inks and the processes of degradation are not yet well understood.

Chemical investigation of inks began more than a hundred years ago, mainly with the aim to improve the quality of inks [5]. In a thorough study of the chemistry of iron gall inks Zetzsche et al. [6] in 1924 prepared a number of model compounds, which they called "primary ink salts". These are mainly iron salts or composites of gallic acid (GA) and pyrogallol (PG) that may be formed by the hydrolysis of tannin (TA) and decarboxylation of GA during ink preparation [6]. More recently, an iron-pyrogallol complex [7] and/or an iron(III) gallate [8] have been considered as the essential colour carrying components of the iron gall inks.

Characteristic features in the range of 1300 - 1470 cm^{-1} and 500 – 600 cm^{-1} in μ-Raman spectra of inks on ancient documents, freshly prepared model inks and GA-Fe composites [9–12] seem to support the idea that an iron gallate is the essential component in inks. However, an unambiguous assignment of these features to particular vibrational modes of iron phenol complexes has not been possible because Raman spectra of possible well-characterized reference materials are missing. In addition, the Raman spectra are more sensitive to the vibrational modes in the organic part of the complexes than to the Fe-O modes which are located in the less resolved spectral range of 400-800 cm^{-1}. A serious difficulty in the characterization of inks is the fact that the colour carrying components are dispersed nanoparticles that are X-ray amorphous [7].

Mössbauer spectroscopy can be a sensitive tool for the investigation of inks on documents and of model systems because it allows monitoring the oxidation state and the electron distribution around the iron atom which is the essential centre of the ink complexes. In addition it does not rely on the crystallinity of the samples. At least in principle Mössbauer spectroscopy is a non-destructive method, which is of importance for the investigation of ancient documents. There are only a few Mössbauer studies of ancient documents [13, 14] and of iron-phenol complexes obtained under conditions similar to those of ink formation [15–21]. Only Burgaud et al. [22] undertook a Mössbauer study of model inks, but these authors investigated only bulk materials of unbalanced ink obtained by total evaporation of reaction mixtures in which additionally the TA had been replaced by GA.

Mössbauer spectroscopy can be used in different ways to study ink related materials: (i) One can study liquid inks as a whole by freezing them and measurements in the frozen state at low temperatures. In this way one gets information on the state of the iron before drying or writing the inks on paper. (ii) One can separate solid materials from the inks by decantation of the supernatant liquid if deposits have formed on the bottom of the vessels, or by filtration or centrifugation. These ink solids can then be washed and dried before the Mössbauer studies. (iii) The inks can be applied to paper and the resulting products can again be studied by Mössbauer spectroscopy in different states of ageing.

Here we report on Mössbauer studies of inks written on paper and of bulk samples obtained by separation of the ink particles by centrifugation or by total evaporation of the reaction mixtures. Frozen suspensions have also been studied. In addition to Mössbauer spectroscopy, we used XRD, IR spectroscopy and chemical analysis to characterize the reaction products. Both balanced and unbalanced inks were studied. The concept of balanced and unbalanced ink has been described by Neevel [23]. It assumes that there is an ideal molar ratio of $FeSO_4{\cdot}7H_2O$ and TA 3.6:1, for a good, i.e., balanced ink. Other ratios are called unbalanced inks and supposed to have inferior properties and be more harmful to the paper on which the ink is written.

We also studied model composites of GA and PG with iron. Mixing polyphenol (PPH) and iron salt solutions always results in a strong decrease of the pH of the solution, making the formation of iron-phenol composites rather difficult. Most isolated materials of this type turned out to be quite different from the materials written on paper. We consider it as more plausible that the latter are ferrihydrite-like nanoparticles perhaps covered by an oxidation product of the PPH.

2 Samples and experiments

2.1 Materials

For the preparation of model inks we used commercial tannic acid (TA; catalogue number 94500) and *gummi arabicum* (g-arabic; catalogue number 63300) from Kremer Pigments and Artist Materials, Aichstetten, Germany. Iron(II) sulfate heptahydrate (henceforth simply called Fe(II) sulfate), iron(III)-sulfate and iron(III)-nitrate nonahydrate from Sigma-Aldrich were used without further treatment. PG (Fluka) and GA (Sigma-Aldrich) were used to prepare model complexes with iron.

2.2 Model for a historical ink

A balanced ink was prepared following a modified ancient recipe given in a manuscript from the year 1500 called the Tegernseer Handschrift (*liber illuministarius*, Bavarian State Library BSB C gm 82 l, fol. 115). Tannin (1.23 g) and *gummi arabicum* (785 mg) were dissolved separately, each in 10 ml of water. The *gummi arabicum* is traditionally added to the ink to improve its adhesion to the quill and later to the paper. The desired amount of Fe(II)-sulfate (720 mg) was dissolved in 5 ml of water. This corresponds to a molar ratio of Fe(II)-sulfate/TA = 3.6:1 if one assumes that the tannin a homogeneous material with molecular weight of 1701 g/Mol, which corresponds to penta(digalloyl)glucose [23].

The solutions of TA and iron sulfate were mixed under stirring at room temperature, which resulted in an immediate color change to dark blue. The *gummi arabicum* solution was added ten minutes later. This ink was applied on groundwood pulp paper (about 70 years old, from the stock of the Bavarian State Library) with a brush a few hours after preparation or one day later.

2.3 Iron composites of tannin, gallic acid and pyrogallol

To get more insight in the nature of the iron-PPH composites, mixtures of Fe(II) sulfate with TA, GA and PG were prepared under the same conditions as the model inks using also the same concentrations of iron sulfate and the PPHs as for the ink samples. The mixing was carried out in air, but without addition of *gummi arabicum*. Since all solutions were highly acidic ($pH \approx 2$), one PPH molecule should be bound per Fe ion [15, 24]. Therefore, most of our experiments were performed with Fe/PPH molar ratios of 1:1. The composites obtained in this way were brushed on groundwood pulp paper. In addition the solids obtained after complete evaporation of the water from the reaction mixtures were investigated. For a better characterization the TA-, GA- and the PG-Fe composites were separated from the reaction mixtures by filtration and centrifugation at up to 9000 rpm and subsequent repeated washing and separation cycles.

To get an insight into the redox behavior of the reacting substances, the influence of oxygen and of Fe(III) sulfate on the composite formation was studied for selected samples.

2.4 Methods

Room temperature Mössbauer spectra were recorded mainly in a velocity range of about ±4 mm/s with a conventional spectrometer using a sinusoidal velocity waveform and a source of ^{57}Co in Rh. Low temperature measurements were performed within a velocity range of about ±10 mm/s in a liquid He bath cryostat with both source and absorber cooled to 4.2 K. Isomer shifts (IS) are given with respect to the source having the same temperature as the absorber and can be converted to shifts relative to α-iron at the temperature of the absorber by adding 0.11 mm/s. The spectra were fitted with Lorentzian lines grouped into quadrupole doublets or magnetic sextets.

3 Results and discussion

3.1 Experiments with frozen solutions

For ink preparation one usually starts with Fe(II) sulfate, but the PPH composite formed contains almost exclusively Fe(III) (cf. Section 3.2). Whereas pure aqueous Fe(II) solutions exposed to air oxidize slowly, the oxidation in the presence of the phenols occurs within about an hour. Therefore, the question arises whether the formation of an intermediate Fe(II)/PPH complex accelerates the oxidation, and whether the often observed Fe(II) site with a QS value of about 2.4 mm/s can be assigned to such a composite as proposed by Jaén et al. [18]. To solve these questions solutions of Fe(II) and Fe(III) sulfate were mixed with solutions of TA/GA or PG, respectively, under exclusion of oxygen.The concentrations of the solutions were as described in Section 2.2; the molar ratios are given in Fig. 1. After mixing the PPH and Fe sulfate solutions a color change to greenish brown occurred but the solutions remained clear. Even during storage for several days no precipitate formed.

To obtain Mössbauer spectra the solutions were frozen by quench cooling with liquid nitrogen and measured at 4.2 K. The Mössbauer spectra obtained for the two solutions are identical (Fig. 1) showing only one sharp Fe(II) quadrupole doublet with a QS $\approx$ 3.4 mm/s, which is the same as the QS of $FeSO_4 \cdot 7H_2O$ [25], which is expected to precipitate when the solutions are cooled. It is interesting to note that Fe(III) is fully reduced to Fe(II) by an excess of PG under exclusion of oxygen. When exposed to air, the solutions turned black and opaque within about an hour. Thus, there is no evidence for Fe(II) complexes with TA, GA or PG. This result is in agreement with the finding of Hider et al. [24] who, for solutions of catechol (CA) and Fe(II) chloride with pH < 5 under similar conditions as in the present case found Mössbauer spectra typical for the Fe(II) hexaquo complex Thus, our findings as well as the results of Hider et al. [24] confirm the statement of Powell and Taylor [26] that there are no PPH-Fe complexes at pH < 7 at least for

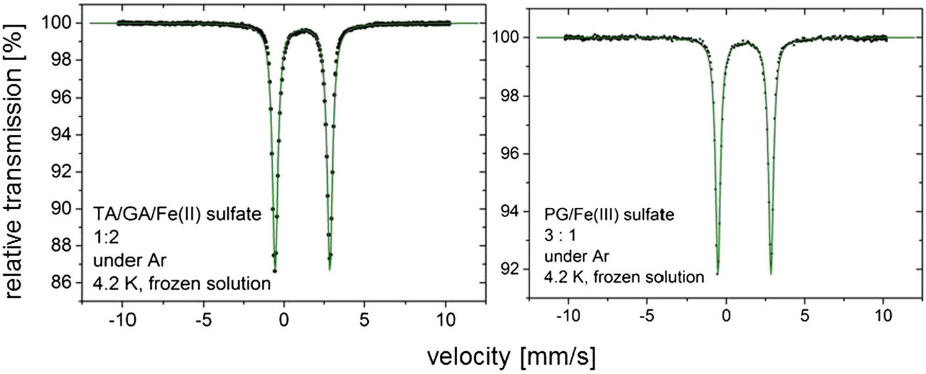

Fig. 1 4.2 K Mössbauer spectra of frozen solutions of TA/GA and Fe(II) sulfate and of PG and Fe(III) sulfate prepared under exclusion of oxygen. Both spectra show only the quadrupole doublet of $FeSO_4{\cdot}7H_2O$. The Fe(III) was reduced to Fe(II) by the addition of PG

PPH = CA, GA, and PG. This interpretation differs, however, from that of Hider [24] who assigned the Fe(II) site with a QS of 3.6 mm/s to a $(CA)Fe(II)(H_2O)_4$ complex. Under alkaline conditions, on the other hand, a Fe(II) gallate complex could be obtained in an anoxic environment [27].

3.2 Isolation and characterization of solid precipitates from PPH-Fe suspensions

After mixing solutions of tannin and Fe(II) sulfate the solution became blue, but remained transparent. Within an hour the solution turned dark blue to black and opaque, presumably due to the formation of finely dispersed particles. Overnight a black precipitate had formed. Parallel to the color formation the pH of the reaction mixture decreased from about 3.3 to 2.9 within a few hours and had reached a value in the range 2.0 to 2.6 in the next morning. The same behavior is observed for mixtures of Fe(II) sulfate with GA and PG, the possible decomposition products of TA [6, 7], independent of the PPH/Fe ratio.

To get more insight into the nature of the TA-, GA- and PG-Fe composites, we isolated the precipitates and the finely dispersed particles. The separation of the dispersed particles of the Fe/PPH composite from the liquid turned out to be rather difficult. Neither by filtration nor by centrifugation at 9000 rpm was it possible to separate the solid completely from the solution. After filtration and drying the solid was so strongly attached to the paper that it could not be removed without contamination with fibers of the paper. Thus only centrifugation was used, which led to supernatant suspensions that were still black, obviously because they still contained colloidal particles.

In case of the total ink the collected precipitate was dried immediately after decantation of the supernatant suspension. In the other cases the solids obtained by centrifugation were washed four times with water and centrifuged after every washing step. The Mössbauer spectra of the dried precipitate of a balanced ink measured at room temperature and at 4.2 K are shown in Fig. 2.

The room temperature spectrum is dominated by a Fe(III) site with a QS value of 1.02 mm/s. Its isomer shift is in the range of about 0.3 mm/s, which is typical for Fe(III) and similar in all other Fe(III) species observed in the other studied inks. In addition there is a significant amount of a Fe(II) site with a QS value of 3.2 mm/s typical for Fe(II) sulfate

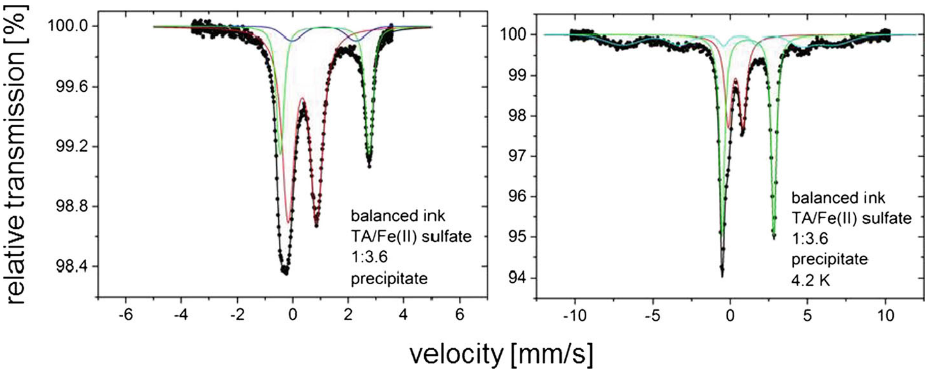

Fig. 2 Room temperature (*left*) and 4.2 K (*right*) Mössbauer spectrum of the *black* precipitate from the balanced ink made of Fe(II) sulfate, TA and *gummi arabicum*

tetra- and heptahydrate [25] and a very broad minor Fe(II) component with a quadrupole splitting of 2.3 mm/s. At 4.2 K the contribution of the sulfate has increased from ∼31 % to 45 % and the QS of this site is 3.36 mm/s (Fig. 2, right). This is again close to the values for $FeSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 4H_2O$ [25]. The increase of the amount of the sulfate may be due to freezing out of adherent iron sulfate solution, or it may be a result of the temperature dependence of the Lamb-Mössbauer factors. In the low temperature spectrum there is also a broad sextet of ferric iron with a mean hyperfine field of 42 T covering 23 % of the spectral area.

The Mössbauer spectra of the solids isolated from mixtures of TA (without *gummi arabicum*) and PG with Fe(II) sulfate (Fig. 3) are dominated by an Fe^{3+} site and look very similar to the Mössbauer spectra of a variety of PPH-iron composites with various tannins, as well as GA, PG and some other PHSs including those of GA and PG observed by Gust and Suwalski [15] and Jaén et al. [16–18]. The TA-Fe composite shows only a single site with a QS value of 1.10 mm/s (see Table 1) corresponding quite well with the QS value of the CII site of various Fe-TA complexes described by Gust and Suwalski [15]. This value is in good agreement with the value of the precipitate from the balanced ink (Fig. 2). The result is also not essentially different for a solid obtained after centrifugation of a TA/Fe(II) sulfate mixtures with a ratio 1:1 except for the residual Fe(II) sulfate hydrates left on the solid because it was not thoroughly washed before drying (see Table 1).

The quadrupole splitting of the Fe(III) component of the PG-Fe composite is 0.83 mm/s which is considerably lower than for the Fe(III) site in the TA-Fe composite (Table 1). Chemical analysis yields a carbon content which is compatible with a 1:1 PG-Fe ratio as found by Krekel [7]. The IR spectrum of this sample resembles that of Krekel.

When the bulk solid obtained from a PG and Fe(II) sulfate mixture was isolated by filtration the remains on filter paper show an Fe(III) site with a quadrupole splitting that is significantly higher (QS = 0.94 mm/s) than for the composite isolated by centrifugation (Table 1). This value is in excellent agreement with the PG/Fe composite obtained by Jaén et al. [18] obtained via the reaction of PG with metallic iron and a PG concentration in the range of our preparation conditions. Almost the same spectrum has been observed for the bulk solid on filter paper obtained from a mixture of PG with a Fe(III) nitrate solution

Table 1 Room temperature Mössbauer parameters for isolated composites of iron with the polyphenols (PPH) tannin (TA), gallic acid (GA) and pyrogallol (PG), and of the respective suspensions written on paper

Sample characterization	Ratio PPH /Fe^{2+}	Fe(III)		Fe(II)	
		QS [mm/s]	A_{rel} %	QS [mm/s]	A_{rel} %
Balanced ink, precipitate	TA/Fe	1.02	67	2.31	7
	1:3.6			3.21	26
Solid, after centrifugation, air dried	TA/Fe	1.05	87	1.67	5
	1:1			2.76	6
				3.19	2
Precipitate, washed, air dried	TA/Fe	1.09	100		-
	1:3.6				
Crust formed during 1 week of evaporation	TA/Fe	0.69	13	3.20	87
	1:3.6				
First precipitate, washed and dried	GA/Fe	0.68	24.4		
	1 : 1	1.08	38.4		
		1.38	38.1		
PG/Fe(II), precipitate, washed, dried	1:1	0.83	90.8	2.47	9.2
PG/Fe(II), suspension evaporated to dryness	1:1			2.75	28
				3.23	72
PG/Fe(II); bulk on filter paper, washed, dried in air	1:1	0.94	89	2.45	11
PG/Fe(III) nitrate, bulk on filter paper	1 : 1	0.96	58	2.34	35
				3.19	7
PG to Fe(II) solution, stirring in air	1:1	1.00	100	-	-
Balanced ink on paper	1:3.6	0.82	62	2.45	38
TA/Fe(II) fresh on paper	1:3.6	0.82	61	2.45	19
				3.19	21
TA/Fe(II) aged 3 d on paper	1:3.6	0.83	71	2.48	24
				3.19	2
GA/Fe(II) on paper	1:1	0.84	82	2.47	18
PG/Fe(III) on paper	3:1	0.84	68	2.51	32
Fe(II) sulfate only on paper	-	0.74	69	2.56	31

(Table 1). If one adds PG in smaller proportions to a stirred solution of Fe(II) sulfate and continues stirring for a few days, the quadrupole splitting is still higher (1.00 mm/s) and reaches values of the TA-Fe composite (Table 1).

In similar materials, Gust and Suwalski [15] and Jaén et al. [16–18] also observed sites with quadrupole splittings of about 0.85 mm/s and 1.1 mm/s, which they assign to Fe-phenol complexes with one and two phenol ligands, respectively.

In the case of the PG-Fe composite there is also a minor contribution (∼10 %) of an Fe(II) quadrupole doublet with QS = 2.47 mm/s. A Fe(II) with a rather similar QS value (∼2.3

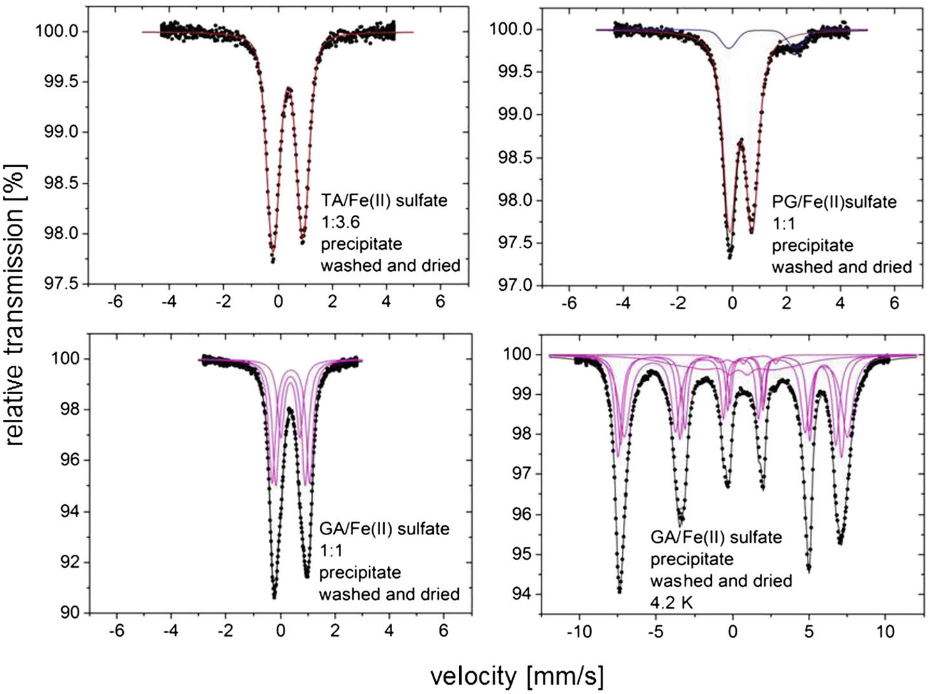

Fig. 3 *Top row*: Room temperature Mössbauer spectra of the washed precipitates from mixtures of TA (*left*) and PG (*right*) with Fe(II) sulfate. *Bottom row*: Spectra of the washed precipitate from a mixture of GA and Fe(II) sulfate recorded at room temperature (*left*) and 4.2 K (*right*)

mm/s) has been observed by Jaén et al. [18] and assigned to Fe(II) composites with phenols. In our Mössbauer measurements of frozen solutions (compare Section 3.1), however, we did not find any evidence for the formation of an Fe(II)-PG complex.

The GA-Fe composite is different. Its room temperature Mössbauer spectrum (Fig. 3, bottom left) can be fitted with a superposition of three Fe(III) sites with different QS values (Table 1). The spectrum looks very similar to the spectrum of the GA-Fe composite described by Burgaud et al. [22]. The 4 K spectrum (Fig. 3, bottom right) shows a well resolved magnetic hyperfine splitting that can be fitted with three sextets with nearly the same hyperfine fields (43.6, 45.3 and 45.2 T) but different quadrupole shifts (-1.20, -0.98 and -0.29 mm/s). The RT as well as the 4.2 K spectra are almost identical with those of an Fe(III) gallate of unknown structure that was obtained from GA and Fe(III) chloride under hydrothermal conditions [27], which suggests that it is the same compound. It is definitely not the Fe(III) gallate whose structure was determined by Wunderlich [8], which shows different Mössbauer spectra both at RT and 4.2 K [27].

However, these isolated solids represent only a minor part of the starting materials in the ink mixtures. In the case of the TA/Fe(II) sulfate suspension only about 200 mg of air dried dry dark blue composite could be obtained from a batch containing 1.23 g TA and 0.72 g of Fe-sulfate (TA/Fe = 1:3.6) after centrifugation and repeated washing with de-ionized water. This material is sulfate free. The Fe content of this sample amounts to 44 mg/g according to chemical analysis. This value is in good agreement with the results described by Zetzsche et al. [6] and the notion that about one Fe atom binds with one molecule of TA with the

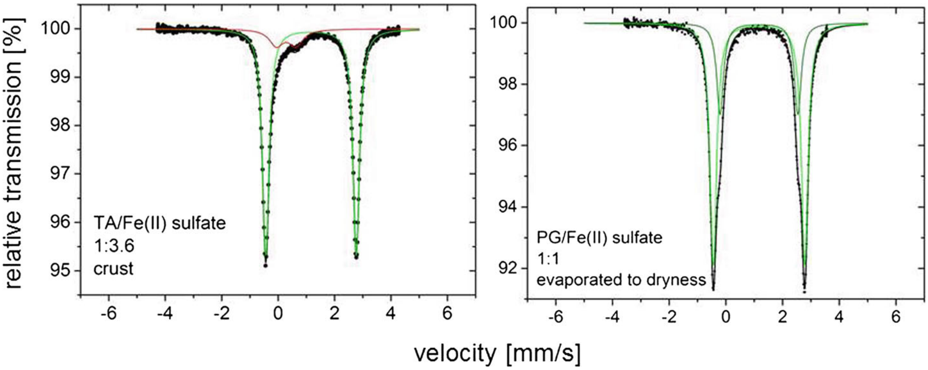

Fig. 4 Room temperature Mössbauer spectra of crust formed on TA/Fe(II) sulfate solution (*left*) and of the PG/Fe(II) sulfate preparation obtained by evaporation to dryness (*right*)

molecular weight assumed by Neevel [20]. The situation is not much different for the GA- and the PG-Fe composites: From the 1:1 batch of the GA/Fe(II) sulfate mixture (1 mmol) only 20 mg of solid was obtained, in case of the PG/Fe(II) sulfate mixture (128 mg of PG and 280 mg of $FeSO_4 \cdot 7H_2O$) the yield was only about 30 mg. Thus most of the starting compounds are left unreacted or form dispersed nanoparticles which could not be isolated by our methods. To prove this suggestion we left the supernatant solutions of the TA-Fe system in an open glass vessel. After a week a thick black crust had formed at the surface of the solution. Evaporation of a small portion of the supernatant solution of the PG/Fe(II) sulfate batch to dryness led first to a dark blue fine powder which turned to a white residue over night. Under the microscope a minor amount of the dark blue phase on the surface of the white material was still visible.

The Mössbauer spectrum of the TA/Fe crust (Fig. 4, left) is dominated by an Fe(II) quadrupole doublet typical for $FeSO_4 \cdot 4H_2O$. The minor component ($\sim$13 %) is a Fe(III) site whose quadrupole splitting could not be determined reliably because of its overlap with the left component of the ferrous doublet. The Mössbauer spectrum of the white solid of the PG-Fe batch (Fig. 4, right) shows two Fe(II) sites with quadrupole splitting values typical for $FeSO_4 \cdot 7H_2O$ or $FeSO_4 \cdot 4H_2O$ (QS = 3.2 mm/s) and the monohydrate $FeSO_4 \cdot H_2O$ (QS = 2.7 mm/s). Thus, most of the iron has not reacted with TA and PG, respectively.

3.3 Model inks and iron-PPH composites (GA, TA and PG) on paper

A typical Mössbauer spectrum of balanced ink (Fe/TA ratio 3.6:1; with *gummi arabicum*) brushed on groundwood pulp paper is shown in Fig. 5 (top left). The fitting results of the Mössbauer spectrum of this ink and other spectra of papers to which ink solutions were applied (Fig. 5) are collected in Table 1. The dominant site in these spectra is always a Fe(III) site. The quadrupole splitting of this site varies in the range of 0.82 – 0.87 mm/s. These quadrupole doublets have always a large line broadening of up to twice the natural linewidth. An additional absorption line at about 2.5 mm/s present in all cases is the right wing of a Fe(II) quadrupole doublet whose counterpart is superimposed with the left component of the Fe^{3+} quadrupole doublet. This Fe(II) doublet is reminiscent of the ferrous doublet observed for the PG-Fe composite obtained as a washed precipitate (Fig. 3, top right) and of a similar Fe(II) doublet observed by Jaén et al. [18] and assigned to Fe(II) composites with phenols.

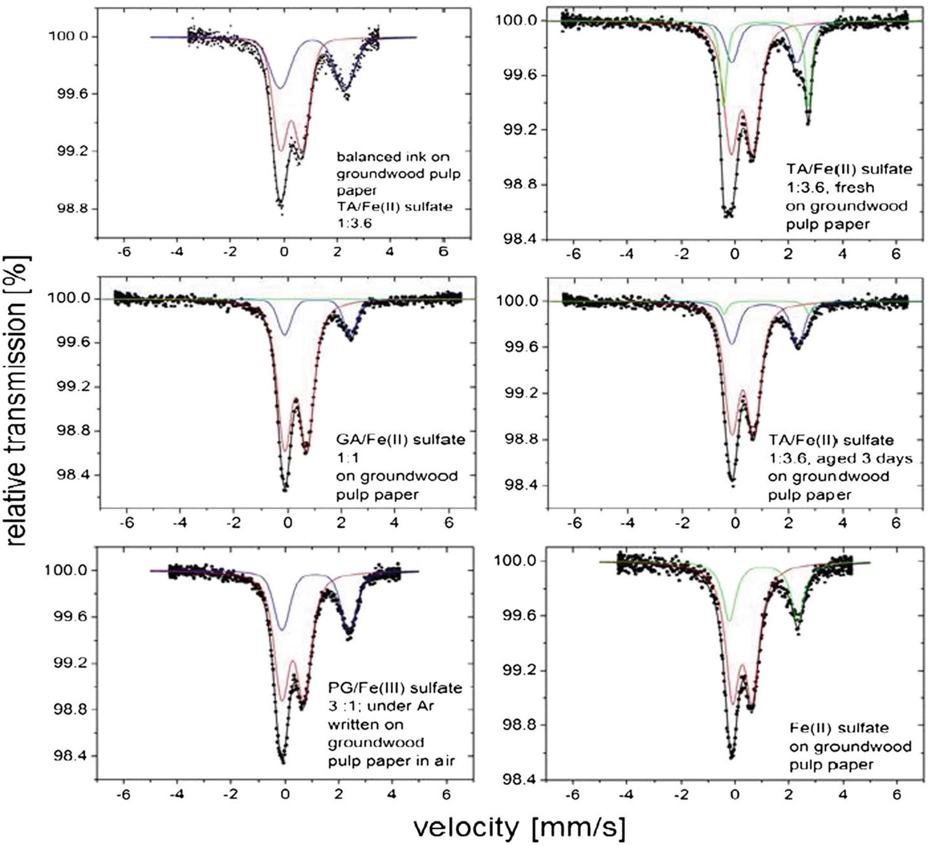

Fig. 5 Room temperature Mössbauer spectra of a balanced ink and TA, GA and PG composites on groundwood pulp paper. For comparison a spectrum of a solution of Fe(II) sulfate only brushed on paper is also shown

These two features have also been found for the TA/Fe composite (1:3.6; without *g-arabic*), but now there is an additional Fe^{2+} site with a quadrupole splitting of 3.2 mm/s (Table 1; Fig. 5, top right). This site can be assigned to a mixture of $FeSO_4{\cdot}7H_20$ and $FeSO_4{\cdot}4H_20$ [25]. When the same TA/Fe(II) sulfate mixture was not written on paper right after preparation but left for 3 days before the application, this contribution decreases from roughly 20 % to less than 5 % (Table 1 and Fig. 5, middle right).

Very similar spectra have been obtained for 1:1 mixtures of GA and PG with Fe(II) sulfate brushed on groundwood pulp paper (Fig. 5, middle left and bottom left). Thus, apart from the Fe(II) site with a QS value of about 2.4 mm/s and a large linewidth the dominant feature is the Fe^{3+} site with a quadrupole splitting in the 0.82-0.87 mm/s range irrespective of the type of the PPH. This value is significantly lower than the value found for the Fe(III) site in nearly all the isolated solids discussed in Section 3.2.

Unexpectedly, an Fe(II) sulfate solution with the same concentration as in the ink experiments brushed on paper shows almost the same Mössbauer spectrum (Fig. 5, bottom right), i.e., an Fe(II) site with a splitting of about 2.56 mm/s and a dominant Fe^{3+} site with a quadrupole splitting of 0.74 mm/s. This ferric component cannot be attributed to a Fe/PPH adduct, because there is no PPH. The QS value is close to that of the Fe(III) sites obtained with the ink mixtures.

The essence of the studies of Fe/PPH composites on paper is that whatever type of PPH (TA, PG, GA) is used, the Mössbauer spectra are always very similar. This is true even without any PPH. This observation raises doubts whether the compounds seen by Mössbauer spectroscopy are, indeed, Fe/PPH complexes.

4 Conclusions

The experiments presented above show unambiguously that the color carrying component of the inks is a rather small fraction of the ink preparation batches. It can be definitely ruled out that it is the Fe(III)-gallate described by Wunderlich [8, 27]. There is also no clear evidence that it is the PG-Fe complex proposed by Krekel [7]. Our results seem to confirm the results of Krekel [7] that below a pH of about 7 only heterogeneous materials can be obtained by the reaction of GA with Fe(II) chloride or Fe(II) sulfate. This is compatible with the observation of Hider et al. [24] that at pH < 5 no Fe-CA complexes are formed and the statement of Powel et al. [26] that under acidic conditions no stable PPH-Fe complexes can be formed. And indeed all specific and well-characterized PPH-Fe complexes are prepared under alkaline conditions.

If there are no specific TA or, more generally, PPH-Fe complexes under the condition of ink formation ($2 <$ pH < 2.5) one must find an alternative explanation for the nature of the Fe species in the iron gall inks. It is worth noting that the QS value of the ink on paper and of the Fe-PG composite is close to the QS values of ferrihydrite-organo-composites [28–30]. The necessity of an alternative explanation is further underlined by the fact that the Fe(II) sulfate written on paper gave almost the same QS value for the Fe^{3+} site as the ink preparations Therefore, we propose that in our TA and other PPH-Fe composites ferrihydrite-like cores are formed which are covered by a polymer of the oxidized PPHs. However, the 4.2 K Mössbauer spectra of our samples do not show the typical magnetic hyperfine splitting of ferrihydrite. This can be considered as a hint that the ferrihydrite-like particles in the inks and the other PPH-Fe composites (the GA-Fe composite seems to be an exception) might be so small that they show superparamagnetism even at 4.2 K. The formation of these complexes could occur in the following way: The dark blue suspensions are formed within about an hour irrespective of the nature of the PPH, whereas the oxidation of Fe(II) in solution takes much longer. The PPHs seem to accelerate the oxidation. Bringing Fe(II) and PPH in contact in the presence of oxygen may start redox reactions which lead to the oxidation of Fe(II), to the oxidation of the PPHs to quinonoid systems and to subsequent polymerization reactions of the PPHs. The decreasing pH stops the reaction and prevents the growing of the iron oxyhydroxide. The PPH polymer covers the iron oxyhydroxide particles and isolates them from the rest of the solution preventing the further growth of the iron oxide nanoparticles. The aggregates formed in this way may be so small that they do not sediment even in centrifugation.

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