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Investigating historical 19th century gel Mediums: from historical recipes to model systems

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Abstract

Gelled mediums were widely used during the 19th century, added to paint on the palette to modify its rheological, optical and drying properties. Many variations of gelled mediums exist in the literature, all with the common basis of mastic resin or varnish, drying oil and a lead compound. With the aim of unveiling the chemistry of such systems, reconstructions were carried out not only following the historical recipes, but in addition, exploring variations and simplifications to get a better understanding of the key ingredients and interactions inducing gelation. Different parameters were tested to establish whether these have an impact on the gelation mechanisms: the influence of the nature and proportions of the ingredients and the preparation process. These reconstructions and their FTIR characterisation reveal the formation of metal-resin soaps, but also underline the specific role of lead in the gelation.

Introduction

The use of gelled mediums was recommended during the 19th century in Britain as additions to modify oil paint properties (Carlyle, 2001a and b). When prepared with oil and varnish some mediums formed a gel-like material. *Megilp* is one of such gelled mediums, made from lead-treated oil and mastic resin varnish. As Carlyle (2001a) points out, although these mediums had become popular with 19th century British artists, one can assume that such recipes were known earlier as all the ingredients would have been present in artists' studios. One first-hand account of their use was in a 1767 notebook belonging to Sir Joshua Reynolds

where he states that he “*varnished with Gum Mast. dissolved in Oil with Sal Saturni*”¹ (Cormack, 1970, cited in Morrison, 2010). This is supported by Joseph Farington, a British painter who describes the use of “macguilp”, “magylph” and “majellup” by himself and his teacher, Richard Wilson, during the 1760s (Carlyle & Southall, 1993).

Chemical analyses of 19th century paintings (Townsend, 1995; Odlyha, 1995; Morrison, 2010) have confirmed the use of such systems by the identification of mastic resin mixed with the oil binder. Townsend *et al.* published an early investigation of reconstructions of gelled mediums; beginning with a survey of published recipes and descriptions of their properties, reconstructions were then prepared with linseed oil treated with lead oxide or lead acetate driers combined with mastic varnish in various proportions (Townsend *et al.*, 1998). The reconstructed gel mediums alone, and mixed into oil paint were then characterised to better identify them in paintings using SEM², FTIR³, TGA⁴, and DTMS⁵.

With the aim of revisiting the chemistry of such systems, reconstructions were carried out not only following the historical recipes, but in addition, exploring variations and simplifications to get a better understanding of the key ingredients inducing gelation (Pasco, 2019). Different parameters were tested to establish whether these have an impact on the gelation process. For instance, one question was whether all the components (oil, triterpenic or polymeric fractions of the resin, and the lead compound) are needed to form the gel, and what is the nature of the impact of their relative proportions and of the addition process.

I. Experimental

a) Materials

Three different “cold drawn” linseed oils were used, purchased from different suppliers (Laverdure, Kremer Pigmente and Schminke). Two different mastic resins were also employed (Laverdure 2015, and Kremer Pigmente 2016), both originally harvested in the island of Chios. To make the varnish, rectified spirit of turpentine from Sennelier was used.

The sugar of lead mentioned in the historical recipes refers to lead acetate (Carlyle, 1999). Lead acetate trihydrate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}_{(s)}$ ($\text{PbOAc}_{(s)}$) (Sigma Aldrich, 99%) was chosen as the closest approximation. It has to be noted that this compound is modified quickly when exposed to air, and partially converts into lead subacetate (Bryant *et al.*, 1984).

¹ Sugar of lead, or lead acetate: the alchemical name of lead being Saturn

² SEM: Scanning Electron Microscopy

³ FTIR: Fourier-Transform InfraRed spectroscopy

⁴ TGA: ThermoGravimetric Analysis

⁵ DTMS: Direct Temperature Resolved Mass Spectrometry

To investigate the influence of the nature of the resin, colophony, sandarac and dammar resins were purchased from Laverdure. Different metallic compounds, from Sigma Aldrich, were also investigated: lead chloride (PbCl_2) lead nitrate ($\text{Pb}(\text{NO}_3)_2$), minium (lead tetroxide Pb_3O_4), hydrocerussite ($2\text{PbCO}_3\text{Pb}(\text{OH})_2$), litharge (lead oxide PbO), and calcium, copper, manganese and zinc acetates (respectively $\text{Ca}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$, $\text{Cu}_2(\text{CH}_3\text{COO})_4\cdot\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$). Oleanolic acid ($\geq 97\%$) and lupeol were also purchased from Sigma Aldrich.

b) Experimental protocol

Detailed protocols were adapted from historical recipes to ensure consistent reproducibility of the reconstructions which could otherwise have been highly variable in terms of the viscosity and texture obtained (Pasco, 2019).

Ibbetson's recipe

A variation of the Megilps (made with lead treated oil and mastic resin dissolved in turpentine to form a varnish), was *Gumtion* which consisted of powdered mastic resin and powdered lead acetate ground together in linseed oil (Ibbetson (1828), cited in Carlyle (2001b) p.394).

Mastic resin was first ground in a mortar: 1 g of mastic resin for 1 min. Then lead acetate trihydrate (0.8 g), hereinafter referred to as $\text{PbOAc}_{(s)}$, was added and the mixture ground again for 1 min. While continuously grinding, linseed oil was then poured in 0.5 mL at a time to a total of 2 g. The mixture was then placed on a slab and ground with a muller over 30 min.

Variations were then prepared with a simplified faster protocol: grinding on a slab with a muller was replaced by grinding the mixture in a mortar (from 1 to 10 min). The different concentrations of $\text{PbOAc}_{(s)}$ range from 9 wt% to 57 wt% (adding from 0.3 to 4 g). Each preparation was then stored in a sealed glass jar.

Model systems

Mastic varnish preparation

A varnish containing 33 wt % of mastic resin and 67 wt % of turpentine was prepared. The resin (15 g) was ground in a mortar and placed in a beaker into which 30 g of turpentine was poured. The mixture was heated to 70°C , and mixed for 15 minutes with a magnetic stirrer. It was then allowed to rest and filtered through laboratory grade filter paper so as to eliminate potential impurities.

Preparation of the mastic varnish + lead acetate mixture:

PbOAc_(s) and mastic varnish were ground together with the following protocol: PbOAc_(s) was first placed in a mortar (between 0.01 and 3 g) and mastic varnish was slowly added (2 g) while continuously grinding for 1 min. The different concentrations of PbOAc_(s) ranged between 2.4 and 60 wt %. The preparations were then each stored in a sealed glass jar.

Removal of the polymeric fraction of the resin

The protocol followed is described in Dietemann *et al.* (2003): first 5 g of mastic resin was ground and placed in a beaker. 15 mL of dichloromethane was added and the mixture stirred until complete dissolution of the resin. 40 mL of methanol was added and a white substance was observed. This polymeric fraction was removed by filtration. After evaporation of the solvents, the remaining fraction was re-dissolved in turpentine.

Preparation of a triterpenoid gel

Two commercial triterpenoids, oleanolic acid (> 97%) and lupeol (Figure 1) were chosen to investigate whether they could form a gel with the following protocol: 50 mg of triterpenoid is added to 1 g of turpentine in a beaker and magnetically stirred. Then the mixture is placed in a mortar and 45 mg of PbOAc_(s) is added and ground for 1 min. The preparation was then stored in a sealed glass jar.

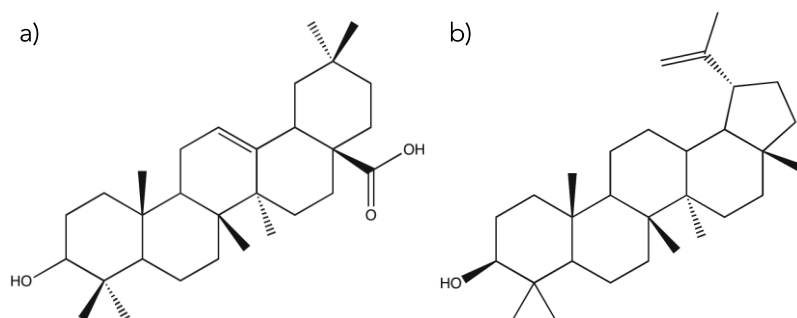


Figure 1: Commercial triterpenoids: oleanolic acid (a) and lupeol (b)

c) FTIR spectroscopy

Multi-reflexion ATR/FT-IR spectra were recorded at room temperature with a *Cary 630 Agilent* spectrometer. For each measurement, three spectra of the same film were recorded - to


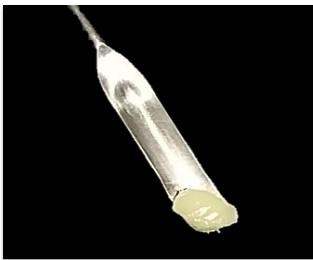
assess the reproducibility - as an accumulation of 32 scans, with a spectral resolution of 4 cm^{-1} .

III. Results and discussion

a) Reconstructions of historical recipes

Many variations of gelled medium exist in the literature (Carlyle 2001b), all with the common basis of mastic resin or varnish, oil and a lead compound. The oil can be any type of drying oil (e.g. linseed or walnut oil) composed of saturated and unsaturated triglycerides in different proportions. Lead can be introduced as powder of litharge (PbO) during the heating of oil, or as powder or saturated solution of lead acetate in the so-called *light Megilp/Gumtion* gels (Table 1). Mastic resin can be added dissolved in turpentine as a varnish, or as a finely ground powder. We focus here on the *light Megilp / Gumtion* formulations. The invention of *Gumtion* is attributed to the artist, painting restorer and author Julius Caesar Ibbetson at the beginning of the 19th century (Carlyle (2001b) p.106-107).

Table 1: Comparison between Megilp and Gumtion recipes, according to the texts reported in Carlyle, 2001a and b.

Components	Brown <i>Megilp</i>	Light <i>Megilp/Gumtion</i>
Drying oil	Cooked with litharge	Raw oil
Mastic resin	In powder or in turpentine (varnish)	In powder or in turpentine (varnish)
Lead compound	Litharge (α -PbO)	Lead acetate
Photographs		

Despite variations in proportions and details, Carlyle identified two main variations in the recipes, substituting mastic resin by mastic varnish and adding water to the lead acetate (Carlyle (2001b) p.107). The original recipe from Ibbetson is reported here:

Ibbetson recipe, 1828 p.16 (cited in Carlyle, 2001b, p. 394-5)

“Take half an ounce of gum mastic, and carefully pick and scrape off every particle of sand or other matter which adheres to it. Add to it a little more than one-third sugar of lead, in

quantity not weight, as the sugar of lead is much heavier than the gum mastic. Grind them together in raw linseed oil. In a short time it will become quite stiff; then add more oil, to make it so thin that it will spread and run on the slab. Take it up in a pot, and grind it again very fine, putting only a small quantity on the slab at once; after which, if it should seem too stiff for use, put a little more oil, and grind it again slightly. A good deal depends on practice, in preparing Gumtion, as well as other paints; but they cannot be ground too fine. ”

Historical recipes quoted in Carlyle (2001b) pp.394-398, give qualitative descriptions of the properties of *Gumtion* and its variations, such as: “*consistency of butter*” (Bulkley, 1821 p.54; Arnald, 1839 p.11), “*white, creamy, opaque compound*” (Reeves and Sons, 1852 p.61), “*white creamy emulsion*” (Edwards, 1856 pp.30- 1), “*opaque mixture*” (Field, 1835 p.208). However, as commonly observed with paint materials, the mixture obtained can vary according to a number of different parameters including whether the mastic resin and lead acetate are introduced as dry powders or predissolved in turpentine or water respectively. The care in preparation, particularly in grinding in Ibbetson’s original recipe also plays a role, “*A good deal depends on the practice, in preparing Gumtion [...]*” (Ibbetson, 1828 p.16, see above).

The first step of this study consisted of an exploration of Ibbetson’s recipe, which is important for understanding the experimental constraints of the preparation of the *Gumtion* and to experience (as the painter would have done) the physical consistency of the material during its preparation, essential to the painter’s final choice. Mastic varnish was first ground in a mortar with lead acetate, then oil was added and ground thoroughly on a slab with a muller over 30 min. An opaque creamy mixture is indeed obtained as specified (Figure 2a).

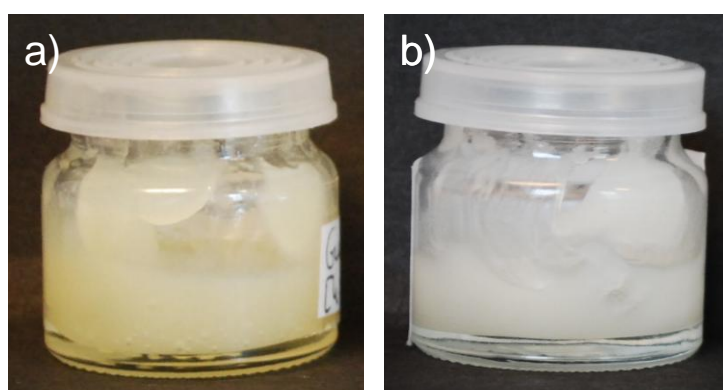


Figure 2: a) Reconstruction of *Gumtion* gels according to Ibbetson’s recipe (oil + mastic resin+ $\text{PbOAc}_{(s)}$); b) “model system”: gel without oil (mastic varnish + $\text{PbOAc}_{(s)}$).

b) Influence of the ingredients

To get a better understanding of the mechanism of gelation, the influence of each ingredient on the formation of the gel i.e., oil, lead and mastic resin/varnish was investigated. To do so, and for all the experiments presented below, a simplified protocol was adopted: ingredients were ground in a mortar (see Experimental section), then placed in a closed vial and the gelation time was identified as the moment when the material no longer flows when the vial is turned upside down (Figure 3).

Mixtures of oil with a lead compound, without resin, do not form gels (although they can be very thick/ viscous formulations); this means that resin is necessary to form a gel. However even without adding the oil, the mixture of resin and lead forms a gel (Figure 2b), as already discussed in Viguerie *et al.*, 2017. Oil is not a pre-requisite for the gelation process, but, as it reacts with lead, it certainly also plays a role in the gelation process and the final structure of the gel. Moreover the addition of oil allows the adjustment of the flow properties of *Gumtion* and subsequently favours its proper mixing with the paint.

Various metallic compounds were experimented with to see whether their nature has an influence on gel formation: different lead compounds (PbCl_2 , $\text{Pb}(\text{NO}_3)_2$, Pb_3O_4 , $2\text{PbCO}_3\text{Pb}(\text{OH})_2$ and PbO) and different acetate compounds ($\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot \text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$). Of these only three allowed the formation of a gel: PbO , Pb_3O_4 and $2\text{PbCO}_3\text{Pb}(\text{OH})_2$ (in addition to the lead acetate called for in the recipes). With these compounds, a homogeneous gel was obtained within few minutes (Figure 3), while the other preparations exhibited two phases and months later still remained in a liquid state (Figure 4). Indeed, the strong ionic character of the bond of the other lead compounds (chloride and nitrate) may limit their dispersion in the organic materials (oil or turpentine and mastic resin). It appears that the acetate function facilitates the reaction between the metal and the triterpenoids. However, the presence of lead seems to be necessary to the formation of an homogeneous gel, as the other acetate compounds without lead do not enable gelation to occur: in the case of $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot \text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, two phases were obtained and analysed via ATR-FTIR.

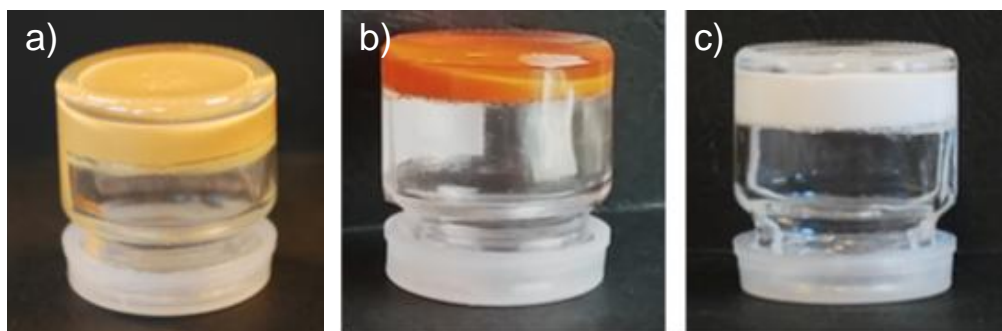


Figure 3: Images showing the preparations that, in addition to $\text{PbOAc}_{(s)}$, will form a gel with mastic varnish: a) lead oxide (PbO), b) lead tetroxide (Pb_3O_4) and c) hydrocerusite ($2\text{PbCO}_3\text{Pb}(\text{OH})_2$).

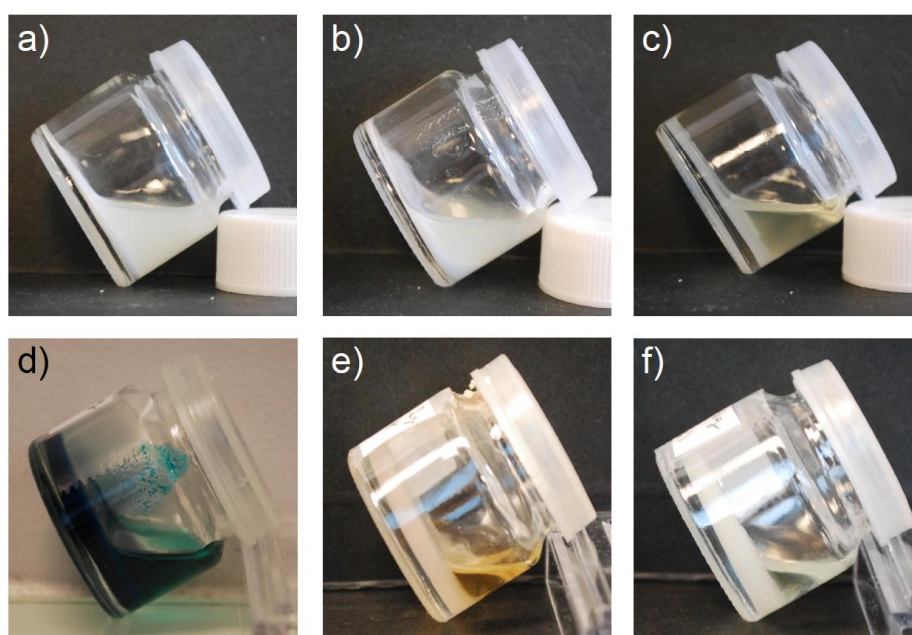


Figure 4: Images showing the preparations that do not form a gel with mastic varnish: $\text{Pb}(\text{NO}_3)_2$, PbCl_2 , $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot \text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (respectively from a to f).

Different resins were then investigated, first dissolved in turpentine and then added to linseed oil and lead acetate trihydrate. Colophony and sandarac (diterpenic resins) as well as dammar resin (triterpenic as mastic resin) were used. Only the mixture containing colophony formed a gel, in contrast to the ones containing dammar and sandarac.

c) Influence of the formulation: proportions and process

The amount of $\text{PbOAc}_{(s)}$ was also varied in two formulations (Ibbetson's original recipe, and the mixture between mastic varnish and $\text{PbOAc}_{(s)}$) to see whether there is a minimum quantity needed to form the gel. In the system without oil, a proportion of $\text{PbOAc}_{(s)}$ of around 2.5 wt% was required to form a gel. In contrast, in the original recipe which includes oil, a higher proportion of the lead compound was necessary (at least 6 wt%).

It is interesting also to see that the amount of $\text{PbOAc}_{(s)}$ has an influence on the gelation time: as one might expect the more $\text{PbOAc}_{(s)}$ was added, the shorter the gelation time. Table 2 presents the results obtained for mixtures without oil.

Table 2: Influence of the amount of $\text{PbOAc}_{(s)}$ on the rate of the gelation of systems containing 2 g of mastic varnish (mastic resin + turpentine).

Weight of $\text{PbOAc}_{(s)}$ (g)	$\text{PbOAc}_{(s)}$ %wt	Gelation time
0.01	0.5	No gelation
0.05	2.4	6 h
0.10	4.8	2 h
0.50	20	15 min
1.00	33.3	10 min
1.50	42.9	5 min
3.00	60	1 min

Systems with oil exhibit much longer gelation time (when ground in a mortar according to the same protocol as the systems without oil); as a comparison, a system containing 20 wt% of PbOAc became a gel in 6 h and a system containing 40 wt% of PbOAc became a gel in 1 h (vs 5 min. for a system without oil).

The preparation processes

Although not always mentioned explicitly, in some historical recipes the importance of the grinding process is highlighted; for example Ibbetson states that the ingredients “*cannot be ground too fine*” (Ibbetson 1828 p.16, see above). The “grinding” step is of great importance in the process: we observed that no gelation is obtained if lead acetate is only mixed with the varnish. To investigate the influence of the grinding process on gelation, tests were carried out with mastic varnish and 20 wt% of $\text{PbOAc}_{(s)}$, with grinding times between 1 and 10 min in a mortar. The gelation time is about 12, 6 and 5 min, when the grinding time is 1, 5 and 10 min respectively (Figure 5), confirming that the grinding time plays an important role in the gelation kinetics: grinding lead acetate to a fine powder increases its surface to bulk ratio probably leading to the enhancement of its reactivity. However, lead acetate has to be ground in the system as air exposure alters its reactivity as we observed grinding lead acetate *prior to* mixing it with the mastic varnish: 5 min grinding first in air leads to gel formation in about 25 min, vs. 5 min to form a gel when the lead acetate is ground directly into the varnish.

Exposing the ground lead acetate powder to air for a few hours before mixing it with varnish extends the gelation time even further (reaching more than 1 h after a 16 h exposure to the air, Figure 5).

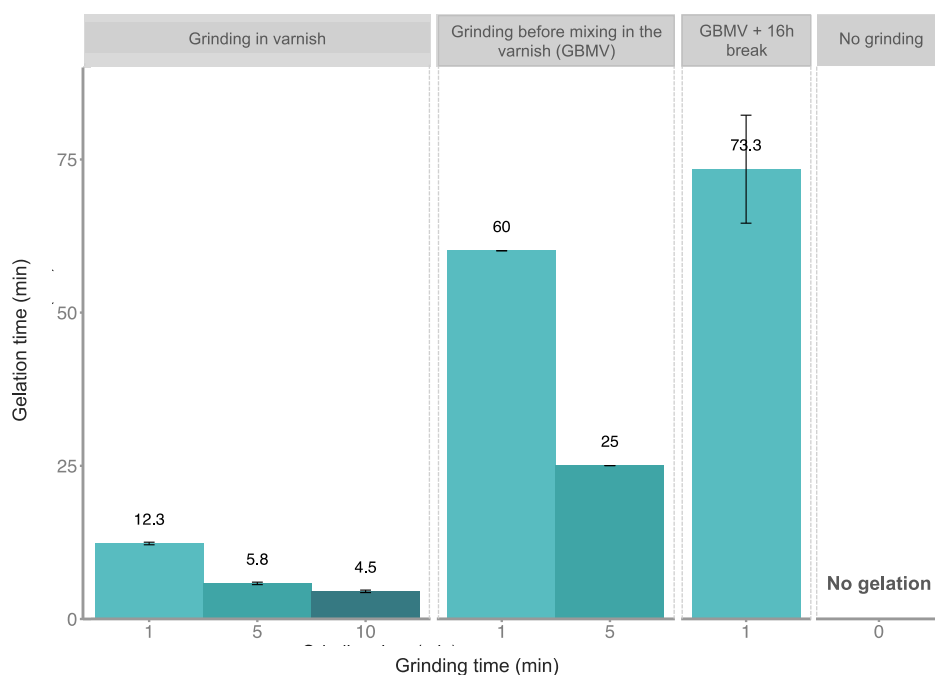


Figure 5: Effect of the grinding process on the gelation time of a system made of $\text{PbOAc}_{(s)}$ and mastic varnish (PbOAc 20 wt%). Each experiment has been repeated 3 times. GBMV: Grinding Before Mixing in the Varnish.

The systems with oil showed the same behaviour, that it is possible to decrease the gelation time by increasing the grinding time. Moreover if the grinding is achieved with a muller, on a slab, and not in a mortar, a gel is obtained much faster and the mixture can be butter-like just after preparation. Most of all, grinding on the slab results in a system that is perfectly homogeneous whereas particles of mastic or lead acetate, which would be very reactive in the system, remain visible when grinding in a mortar only. When mixed with oil paint the presence of these particles in the medium could raise issues of long-term conservation.

d) Model systems to understand the gelation process

Polymeric part

To investigate which part of the mastic resin is involved in the gelation process, the polymeric fraction of the resin was removed, following the protocol described in Dietemann (2003). After removing the poly- β -myrcene from the mastic resin, a “triterpenoids varnish” was prepared adding turpentine, and ground with $\text{PbOAc}_{(s)}$: a thick white gel was obtained very quickly, less than 1 min. It shows that the gelation depends on the interaction between the

triterpenoids and the $\text{PbOAc}_{(s)}$. As in the case of the oil, the polymeric part of the resin does not seem necessary to form the gel, but might have an impact on the gel texture.

Nature of the triterpenoid

Subsequently, two commercial triterpenoids known to be present (or at least structurally close) in mastic resin - oleanolic acid and lupeol - were used to investigate whether they also can form a gel (Figure 1). In the case of oleanolic acid, thick, opaque and white gels are obtained within a few minutes to 2 h, depending on the amount of lead compound present. In contrast, and despite the similarity of its structure to oleanolic acid, when lupeol is used as the commercial triterpenoid, no gelation is observed. One important difference between these two compounds lies in the presence of a carboxylic acid group, which may thus play a role in the gelation process: this observation suggests that the gel forms thanks to the interaction between the carboxylic acid functional group of the triterpenoids and the lead compound.

e) FTIR study

All formulations were analysed via FTIR spectroscopy. To shed new light on the gelation mechanism and confirm the previous assumption, we can focus first on the simplified formulations with mastic and $\text{PbOAc}_{(s)}$ (figure 6a and individual components in Figure S1): the FTIR spectrum of the mixture “mastic resin + turpentine + PbOAc ” shows the presence of two bands at 1576 and 1514 cm^{-1} in the range of carboxylates (asymmetric band). They can be inferred to the interaction between lead and the acidic part of the resin with subsequent lead-resin soap formation. The formation of lead-resin soaps has also been shown by Poli *et al.* (2019) in paint mixtures containing resin and a metal-based pigment. A shoulder visible around 1410 cm^{-1} may be then assigned to the carboxylate symmetric band. To confirm that the band at ca. 1520 cm^{-1} is not due to remaining $\text{PbOAc}_{(s)}$, we reproduced the experiment analysing the same mixture but with PbO (instead of $\text{PbOAc}_{(s)}$) which does not present any feature in this range. The FTIR spectrum of the gel obtained (figure 6b) clearly confirms the presence of a band in the range of carboxylates that cannot be inferred to any individual component. One can also see the presence of the mastic resin carbonyl stretching band (ca. 1710 cm^{-1}), since the resin contains a lot of carboxylic acid and ketone groups; this band does not undergo noticeable change when the lead compound is added, suggesting that only a few carbonyl moieties interact with the lead. A small shoulder of the large carbonyl massif is also present at ca. 1750 cm^{-1} that can be assigned to the new chemical environment in the mixture.

FTIR spectra of the model system composed of oleanolic acid and a lead compound are presented in Supplementary Information. Similar observations can be made with the formation of new carboxylate species in the system confirming the reaction between triterpenoids of the resin bearing acidic functions and the lead compound. These spectra are detailed in Pasco *et al.* (2021) with details on the possible structure of the lead-oleanolic acid complex.

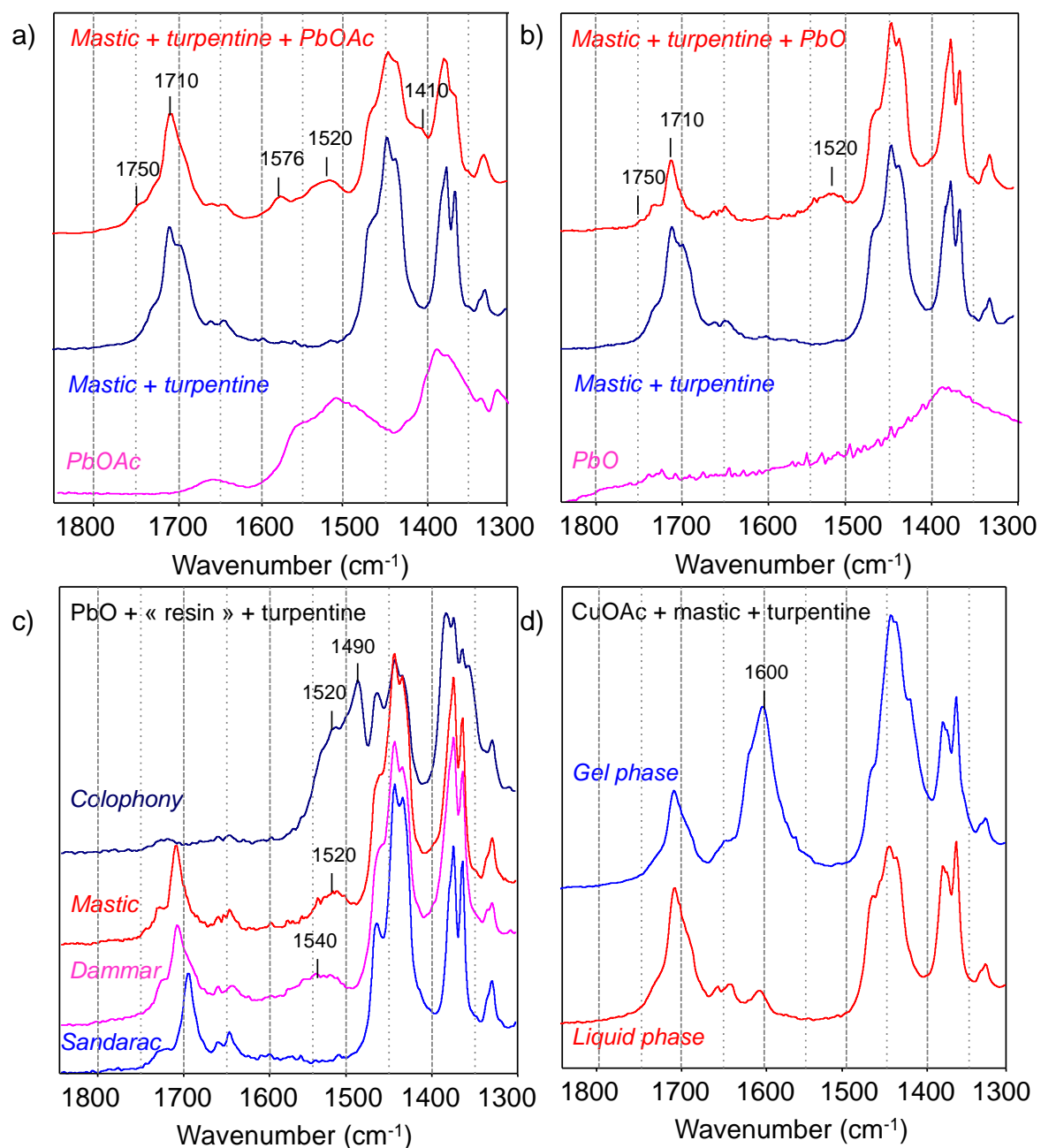


Figure 6: ATR-FTIR spectra of a) $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ($\text{PbOAc}_{(s)}$) (pink), mastic varnish (blue) and the corresponding gel, with $\text{PbOAc}_{(s)}$ 33 wt% (red); b) PbO (pink), mastic varnish (blue) and the corresponding gel with PbO 33 wt% (red); c) mixtures of varnishes (resin + turpentine) and PbO 33 wt%; d) mixture of mastic varnish (mastic + turpentine) and $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot \text{H}_2\text{O}$ (CuOAc) 33 wt%.

FTIR spectra of the preparations based on the historical recipes, with oil, mastic and lead acetate, also show this carboxylate band around 1520 cm^{-1} . This is difficult to interpret without the results from the simplified formulations (as noted in Townsend *et al.* 1998; Viguerie *et al.* 2017). It is interesting that the band is much more intense when the materials were ground together with a muller: the difference in the preparation process not only modified the texture and homogeneity of the system but also its chemical composition (and thus probably the structure and stability of the gel). As this band is quite large, it is not possible to state whether it has to be inferred only to the interaction of lead with resin or also with oil (lead soaps commonly found around 1530 cm^{-1}). A possible contribution of lead soaps or even mixed lead oil-resin soaps cannot be discounted and requires further investigation. This opens-up a wide area of research in order to better understand the reactivity of such systems, possible interactions within a painting, and competition between resin- and oil-soap formation.

FTIR spectra of the mixtures of different resins and lead oxide (PbO) also provide unexpected information (Figure 6c). Formulations containing colophony also present a band in the range of carboxylates, very intense compared to the one obtained with mastic. It should be noted that the carbonyl band completely disappears in that case which would indicate that all the resin is involved in the carboxylate formation. More surprisingly, formulations containing dammar exhibit a broad band in the “soap” region, although a gel is not formed when this resin is employed in the preparation of gelled mediums. Sandarac resin seems less reactive as no band appears when it is used with PbO.

We also investigated the two phases which were obtained after grinding Cu, Mn and Zn acetates with mastic varnish. One example is given, with the mixture of mastic varnish (mastic + turpentine) and CuOAc, in Figure 6d: the lower “jelly” phase was compared to the upper liquid phase. Here again carboxylate bands are clearly visible in the “jelly” phase, due to the combination of the acid present in mastic resin and the metal acetates. In this case, although the soap band is high, the carbonyl seems almost unaffected. Despite the carboxylate features present in the jelly phase, it is interesting to note that these acetate compounds with Cu, Mn and Zn did not form homogenous gels. This investigation also indicates, that similar to the case with dammar–lead mixtures, the formation of soaps alone is not enough to form a gel; the gelation process requires the specific properties of lead (Pasco *et al.*, 2021).

Conclusion

In summary, different variations of traditional recipes, based on oil, mastic resin and a lead compound, have been found to form a gel. Mixtures without oil do form a homogeneous gel, as well as systems prepared with colophony instead of mastic resin. Of all the metallic compounds investigated, only Pb compounds allow the formation of homogeneous gels, i.e., lead acetate, litharge (lead oxide), minium and lead white. Other acetates (based on copper, manganese or zinc) induce the formation of two phases, as well as the use of dammar or sandarac resins. According to these reconstructions and to their FTIR characterisation, the gelation process is based on the interaction of the acidic part of the terpenoids of the resin with the lead compound, forming lead-resin soap species. These carboxylate species are also found in unstable systems (presenting two phases) showing that their formation is necessary but not sufficient to ensure complete gelation.

While lead (-oil) soaps are widely described in the literature and studied by numerous groups with possible associated degradation defects, these lead-resin soaps were only recently highlighted in paintings (Poli *et al.*, 2019). Further investigation would be required to evaluate the long-term consequences of the presence of these species in the complex paint system. The exact role of oil would also have to be further investigated: although the oil is not necessary to form the gel, it may also be involved in the gelation process. Indeed, adding oil to the system should induce the formation of lead soaps or even “mixed” carboxylates (from a possible interaction oil-lead-resin).

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