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Historical evolution of oil painting media: A rheological study

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Abstract

Rheology is the science of flow, which is a phenomenon found in every painting operation, such as decorative paintings or protective coatings. In this article, the principles of rheology as applied to paintings and coatings are recalled in a first part and the rheological criteria required in the paint industry presented. Indeed, different flow behaviours leads to different finishes. The same procedure and techniques as in industry can be employed to explain some evolutions in oil painting aspects over the centuries. The first recipes for oil painting indicate the use of treated oil, resins and spirits. This article deals with the evolution of the composition of these systems as media for oil painting, according to rheological clues.

During the Renaissance period, the media used were Newtonian or slightly shear thinning and allowed one a perfect levelling. Then techniques changed, paints became more opaque with less addition of oil/resin media, and brushstrokes appeared visible. Some preparations containing lead, oil and mastic resin, whose flow behaviour is closed to those required in industry, may have appeared during the 17th century and are still used and sold today. ***To cite this article: L. de Viguerie et al., C. R. Physique 10 (2009).***

Résumé

Histoire des médiums et liants pour la peinture à l'huile : étude rhéologique. La rhéologie, science de l'écoulement, est à ce titre présente dans toute opération de peinture. Nous proposons dans une première partie un bref rappel des principes et définitions en rhéologie ainsi que les différents critères définis dans l'industrie pour la formulation. Les propriétés rhéologiques conditionnent en effet le rendu final de la peinture. Un même type de raisonnement peut être appliqué tant pour la mise au point des peintures industrielles où il s'agit d'ajuster la formulation en fonction des critères requis, que pour l'étude des peintures de chevalet où le rendu final donne des informations sur la rhéologie et donc la composition de la peinture utilisée. Les premières recettes de liants et mediums pour la peinture à l'huile indiquent l'utilisation d'huile, de résines, et d'essence. En partant de l'étude rhéologique de ces systèmes nous proposons de suivre l'évolution de leur composition et de leur utilisation en tant que médiums pour la peinture à l'huile.

Pendant la Renaissance, des systèmes newtoniens ou légèrement rhéofluidifiants permettant un nivellement complet de la surface, ont du être utilisés. Progressivement les techniques se modifient : la touche de l'artiste devient visible. Les traces de pinceaux apparaissent, la peinture est utilisée opaque (et non plus transparente en glacis) et les mediums huiles/résines sont moins employés. Des préparations à base d'huile additionnée de plomb, et de résine mastic apparaissent, au XVIIe siècle d'après certaines sources.

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Ces préparations, dont les propriétés rhéologiques sont proches de celles recherchées par l'industrie, sont encore préparées et vendues de nos jours. ***Pour citer cet article : L. de Viguerie et al., C. R. Physique 10 (2009).***

Keywords: Rheology; Oil painting; Levelling; Drying; Brushstrokes

Mots-clés : Rhéologie ; Peinture à l'huile ; Nivellement ; Traces de pinceau ; Séchage

1. Introduction

For centuries painters have been experimenting with paint formulae and adjusting consistencies according to the effects they expected. Knowing the rheological properties of the paint is crucial to painters to predict the behaviour during and after application, and thus the visual aspects they will obtain. From the art historian's point of view, simple observations of a painting's finish may allow one to describe the rheological properties of the paste used. In some cases, making the composition known is even possible.

The rheological properties of paints are widely studied in industry. The same criteria as those defined by modern industry (conditions for good levelling and brushability, but without sagging) can be applied as a way to find clues for the reconstruction of old recipes.

In this article, after recalling the methodology developed for industrial applications, we will first focus on early-developments in oil painting media. As Renaissance painters carried out in-depth research on new painting formulation, it is interesting to study the influence of these techniques that appeared during the 15th century. Different ingredients and formulations have been used and simple reconstitutions were made to describe their rheological behaviours.

Seen in this way, the evolution of oil painting medium will be charted through rheological observations. The visual aspect of masterpieces has changed over the centuries, from Van Eyck to Rubens; obviously the properties required for paints have also changed! Painters from the 19th century tried to re-constitute the old secret formulations and particularly that of Rubens' medium which was believed to be the 'ideal medium'.

2. Rheological properties of industrial paints

2.1. Different types of viscosity behaviour

Viscosity is, by definition, the ratio between the shear stress and the shear rate. It expresses the resistance of a material to flow [1]. The rheological profile, meaning the dependence of the viscosity with the shear rate, defines most paint flow properties. A painter would, however, use the term 'consistency' to refer to the rheological properties of his pastes.

The paint industry has extensively studied the behaviour of different paints, presented in Fig. 1. Newtonian or ideal flow behaviour, in which the viscosity is independent of shear rate, is common for solvents, resins, varnishes and many industrial coatings. When the viscosity decreases as shear rate increases, the system is called shear thinning. In some cases, the system does not flow at rest but a minimum force has to be applied to make it flow: this minimum force is called the yield stress. A shear thinning system with a yield stress is plastic: this will be the case for pigment pastes, trade sales paintings and some coatings.

Another form of behaviour can be defined if time is considered: in thixotropic systems the viscosity decreases with time under shear. When the shear is stopped, the viscosity recovers with time. Thixotropy is often confused with plasticity whereas the former is time and shear rate dependent and the latter is only shear rate dependent [2].

2.2. What are the criteria for ideal painting in industry?

The paint industry conducted research and tried to develop criteria and methodology for an ideal wall painting [3–7]. Since different events during the application and the drying of a paint layer are associated with different shear rates [7] (Table 1), the flow properties of a paint has to be tested over a wide range of shear rates and not at a single point.

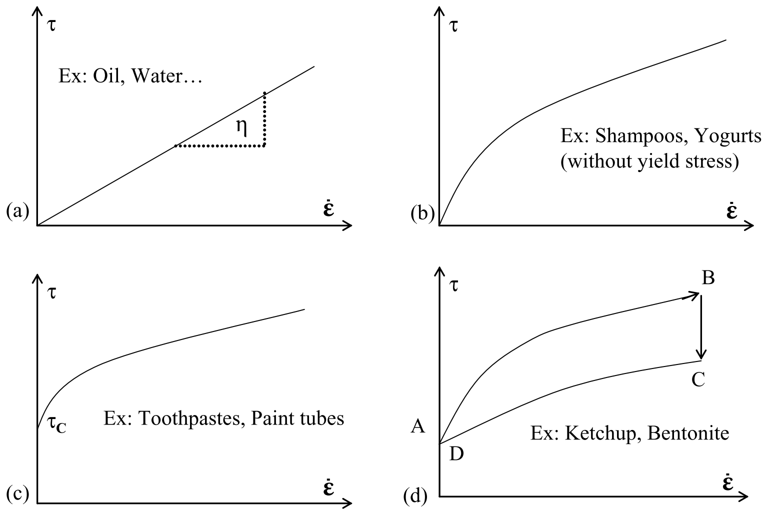

Fig. 1. Various flow behaviours: shear stress (τ) depending on shear rate ($\dot{\varepsilon}$). (a) Newtonian behaviour: the viscosity is independent of shear rate. (b) Shear thinning behaviour: the viscosity decreases as shear rate increases. (c) Plastic behaviour: shear thinning system with a yield stress (τ_C). (d) From A to B, the viscosity decreases as shear rate increases. Thixotropic behaviour: from B to C, the viscosity decreases with time at constant shear rate. From C to D, the shear rate decreases: point D is the same as A for thixotropic systems.

Table 1
Ranges of shear rates associated with the different events that occur during the application and the drying of a paint layer.

Event	Rest/settling	Levelling/sagging	Brushing
Shear rate (s^{-1})	10^{-3} to 10^{-2}	10^{-2} to 10^{-1}	$> 10^2$

A good paint must be easily spreadable but must not sag. Moreover, the surface quality of the finish depends on the ability of the liquid film to level the irregularities generated during the coating process [5,8]. The paint industry has to achieve different objectives that can seem paradoxical. At high shear rates, a low viscosity is beneficial for brushing and spraying: a too high viscosity may lead to undesired brush drag [6]. Good brushing properties are obtained if the viscosity at high shear rates does not exceed 0.2–0.5 Pa s. At a very low shear rate, sagging will be avoided for high viscosity fluids, but here the viscosity has to be controlled to achieve a good levelling. Flow out of the applied film is facilitated by low viscosity (under 0.2–0.3 Pa s at low shear rates), maximum film thickness, and by low or zero-yield value [3].

A combination of plastic or pseudoplastic and thixotropic behaviour (i.e. shear thinning and recovery of the plastic or pseudoplastic properties after flow cessation) is formulated into trade sale paints, gel coats and water-borne paintings and gives quite good results: low viscosity at the high shear rates of processing and application, followed by a viscosity or yield stress recovery when the shearing stops. As explained in [8,9], this behaviour is desirable because it combines pigment stability with excellent flow properties, hence easy brushability without sagging, good levelling properties and good workability, as it is possible to superimpose a new layer of paint on a previous one when the first is not completely dried. Moreover, in the 1960s, thixotropy was considered as one of the most striking progress in the technology of this industry since 25 years [9].

3. The first recipes for oil painting

At the very beginning of European oil painting, Flemish painters used to apply transparent glazes of various thicknesses over opaque or semi opaque underlayers. This glaze technique allowed them to obtain optical effects, model the forms and create a sense of depth and relief. The same effects were not possible with the previous painting techniques, such as tempera (Fig. 2), which made the colours appear more or less opaque [10]. Glazes are thin translucent layers, rich in medium, with low pigment content. As the pigment content is very low in the final glazes for modeling

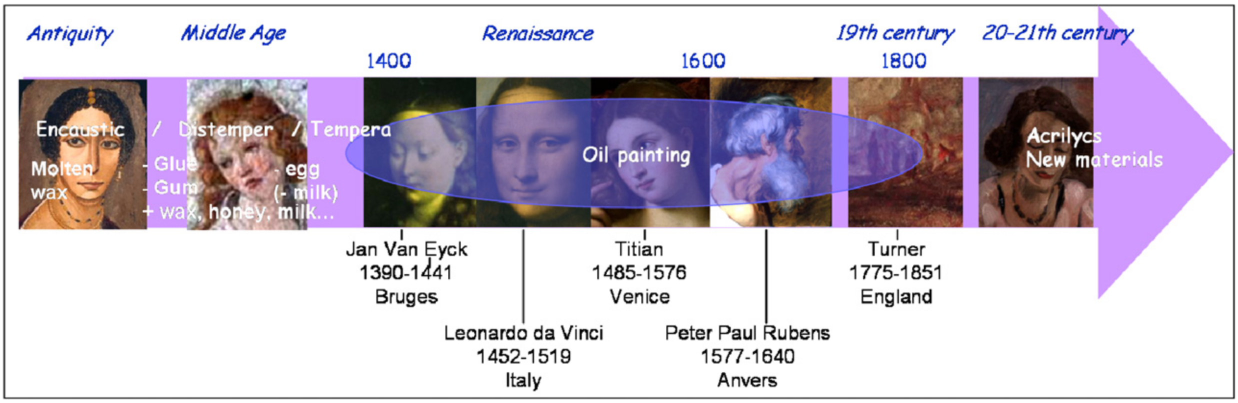

Fig. 2. Timeline presenting the main techniques in Europe and painters cited.

Table 2
Rheological behaviour of the main components of glaze medium formulations. Oils containing a low amount of litharge (less than 10%) could exhibit thixotropic behaviour.

Formulation	Rheological behaviour
Mastic (<70%) + oil + turpentine	Newtonian
Mastic (>70%) + oil + turpentine	Slightly shear thinning + existence of yield stress
Oil + litharge	Thixotropic
Oil + litharge ⩾ 20%	Shear thinning (*Thixotropic*?) + yield stress ≈ 200 Pa
Oil + litharge, addition of water during heating	Thixotropic, higher viscosities, no yield stress (even ⩾ 20%)

shadows in the flesh tones, we make the assumption that the rheological properties are due to the binder behaviour and we will focus only on the binder formulation.

What were the possible ingredients? What would be their rheological behaviour and is it compatible with the finish obtained by Renaissance painters? The influence of each possible ingredient has been studied separately and the results are summarized in Table 2.

3.1. Experimental

3.1.1. Reconstitutions of old recipes

Preparation of varnishes

The oil used is linseed oil, cold-pressed, from Laverdure (Paris, France). The mastic resin was Chios mastic, purchased from Okhra (France), and the turpentine from Laverdure. Several amounts of resin, from 20 to 80%wt weight of resin, were studied to evaluate the effect on the viscosity. The resin was first ground in a mortar and then placed in a beaker. The appropriate quantity of turpentine or oil was added and the mixture was heated at 100 °C, under continuous manual stirring. For turpentine varnish, the heating time was 5 min, whereas for oil varnish, it was necessary to heat 20 min to obtain homogeneous mixtures. Varnishes were then filtered so that potential impurities were eliminated.

Preparation of heated oils with litharge (recipe from [11,12])

The litharge, PbO (Interchim Montluçon, France), and the raw oil (linseed and nut oil, Laverdure), were mixed thoroughly by grinding the litharge in the oil, as it is done for the preparation of colours. To study the effect of the amount of lead oxide on the texture, several preparations containing various amounts of litharge, from 0%wt to 20%wt, were tested. The litharge is first added to a little quantity of oil (few droplets) and ground in a mortar. The rest of oil is then added to the mixture and put in a beaker where the preparation is heated at 150 °C for two hours under continuous magnetic stirring.

Oils heated with litharge in presence of water were also prepared. Our reconstructions were made by heating a mixture of water, oil, and litharge at 100 °C for two hours. At regular time intervals, each 15 min, water was added so that the final quantity of water introduced equals the quantity of oil. After heating, the aqueous phase was separated by settling, and rheological measurements were performed on the organic phase.

Preparation of a Flemish medium (from [12])

The following mixtures were first prepared as described above:

- Mastic varnish containing 60%wt of resin mastic and 40%wt of turpentine.
- Heated oil with 10%wt of litharge (without water).

Then they were mixed in the same proportions and stirred manually.

Preparation of the megilp: Templeton's recipe [13]

A saturated solution of lead acetate $Pb(C_2H_3O_2)_2$, $3H_2O$ (4 g) was added to linseed oil (8 g, the double amount) and mixed vigorously. Then 8 g of mastic varnish previously prepared, containing 30%wt of resin mastic and 70%wt of turpentine, were also added under continuous manual stirring.

3.1.2. *Rheological measurements*

The viscosity measurements were performed at 25 °C from 0.04 to 2000 s^{-1} in order to characterize the systems on the whole range of shear rates that have to be considered, corresponding to the different events during the application and the drying of a paint layer (Table 1). Dynamical and flow measurements were performed. Flow properties were investigated with a strain controlled rheometer Rheometric (RFSII) equipped with a cone and plate geometry (diameter: 25 mm; angle: 0.04 radian; gap: 43 μm) composed of titanium and stainless steel respectively, or a stainless steel coaxial cylinders (inner cylinder diameter: 16.5 mm; outer cylinder diameter: 17 mm; length: 13 cm).

Yield stress of the oil treated with the highest amount of lead (4:1), and dynamical properties were measured using stress controlled rheometer Haake RS600 equipped with a stainless steel cone and plate geometry (diameter: 35 mm; angle: 0.04 radian; gap 103 μm).

Each measurement was repeated twice to check the reproducibility. Another sample with the same composition, prepared in the same conditions, was also analysed and its properties compared to the first one. Indeed, two samples with the same composition present similar behaviour, but the exact values of viscosity or yield stress can vary slightly: a maximum deviation of 30% can be found.

3.2. *Results: the rheological properties of the main components*

3.2.1. *Oils*

The Van Eyck brothers (Fig. 2) have long been thought to be the first to discover the properties of siccative oils to form a tough film after exposure to air [14]. This would have been the beginning of European oil painting, born with the Flemish Rennaissance painters, and then vehiculated to Italy by Antonello da Messine. Actually, it is now well known that oils had been used before, at least for varnishes. A visual change occurred in paintings at this time, which has been thought to be linked to the apparition of prepared oils as binders.

Linseed oil, as nut and poppy seed oil, were commonly used at this time. These drying oils are characterized by high levels of polyunsaturated fatty acids, mainly linolenic acid for linseed oil, and linoleic acid for nut and poppy seed oils [15]. The double bonds of the unsaturated acids confer their chemical reactivity and allow them to react with the oxygen of air and with one another to form a polymeric network. The drying mechanism of linseed oil is still far from being completely understood. It is generally considered to be due to a process of autoxidation followed by a polymerisation [16].

Oils, before being mixed with the pigments, are submitted to pre-treatments that enhance and fasten this process. Old recipes indicate various methods which have not dramatically changed over the centuries. Thickening the oil by placing it in the sun, or heating it with a lead compound was often advised. The addition of lead, especially lead oxide (gold litharge), in the preparation of drying oils has been commonly used and reported in numerous recipes [11,12,17].

Pure oils are all Newtonian with a rather low viscosity, around 0.04 Pa s.

As indicated in a previous study [18], the addition of lead oxide modifies the colour and the rheological properties of the medium. In presence of lead, the heating produces brown–black mixtures. The oils are no longer Newtonian

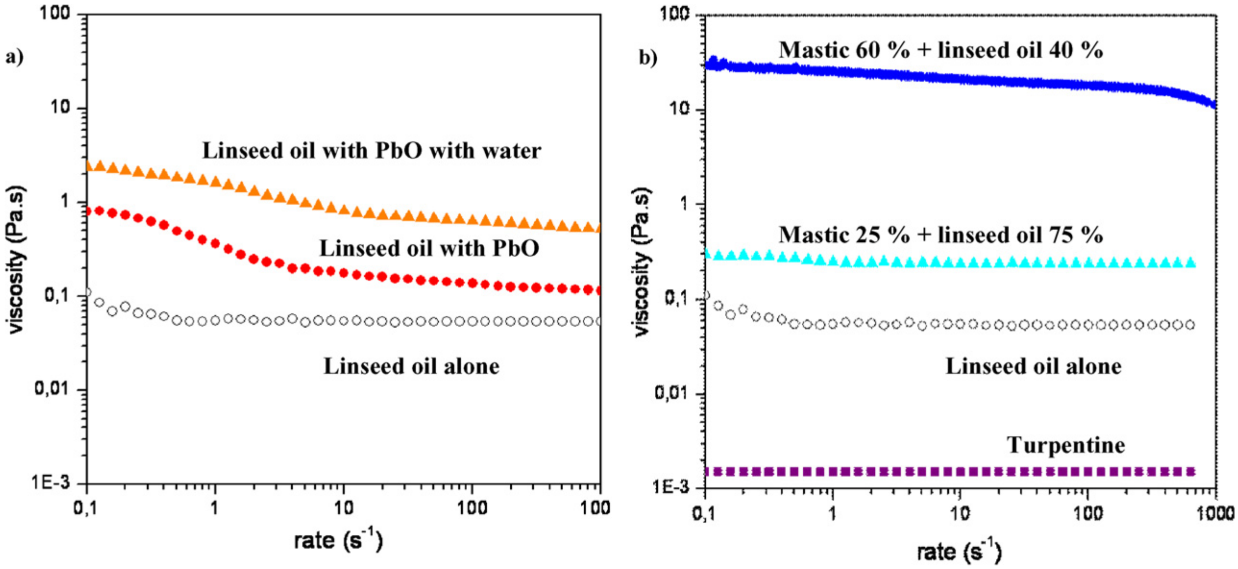

Fig. 3. Rate sweep test of various preparations: (a) pure linseed oil (○), linseed oil heated with litharge (10%wt of lead) with (▲) and without (●) water during the heating process. (b) Turpentine (■), pure linseed oil (○), linseed oil + 25%mastic (▲), and linseed oil + 60%mastic (●).

but shear thinning, and the viscosity is increased over a wide range of shear rates as seen in Fig. 3a. Moreover, these systems are also time dependent with a delay in the viscosity recovery, particularly for those containing a high amount of litharge (higher than 10%wt). This thixotropic behaviour corresponds to a medium that is very viscous on the palette, flows under the brush (or the painter's fingers) and provides better levelling properties. However, the delay in the viscosity recovery is too long to permit the superposition of an upper layer before the previous one has dried.

It has also to be noted that a medium obtained with a high amount of lead oxide above 20%wt does not flow during storage: a plastic system is formed with a yield stress estimated around 200 Pa. For this amount of lead, the viscosity recovery (with the existence of yield stress) could not be observed in two years after shearing.

According to Maroger [12], Leonardo da Vinci improved this process by adding water in the mixture to prevent the dark colouration of the oils obtained. The ebullition allows a better stirring and a limitation of the temperature. Indeed a better colouration is obtained (Fig. 4a/b), and as water enhances the saponification [19], the viscosities are increased for a same content of lead. However, it does not modify the rheological property of the medium for a lead content less than 20%wt, as seen in Fig. 3a. The only remarkable change is that the medium containing 20%wt of lead does not exhibit any yield stress if the heating was done with water.

3.2.2. What about adding resin?

One of the first indications of the use of drying oil for paintings was found in the Lucca manuscript (8th century) and concerns the mixing of oil and resin to make varnish. For a long time, oils were only used mixed with resins for varnishes (i.e. without pigments) before being used as a binder. One can thus assume that the first painters who had the idea to grind pigments in siccative oils also added resins. The resins used at this time were natural resins, such as colophony, sandarac, and mastic.

Resins consist of di- or tri-terpenoids together with a proportion of a polymeric material. Mastic resin, a natural resin from trees of the Pistacio family, consisting of tri-terpenoids [20] is used in our reconstitutions.

The preparations made of mixtures of pure oil and resin mastic are all Newtonian. Their viscosity increases along with the concentration of resin (Fig. 3b). Thus, with a high quantity of resin, the mixture is very viscous and not easily spreadable. The medium does not flow any longer if the resin content exceeds approximately 70%wt. Under this value the addition of resin does not modify the rheological behaviour of the mixture and just increases the viscosity. Moreover, the drying time remains quite similar. The mechanisms involved are rather complex but it can be considered that, as for oils, the drying process is led by oxidation and cross-linking [21].

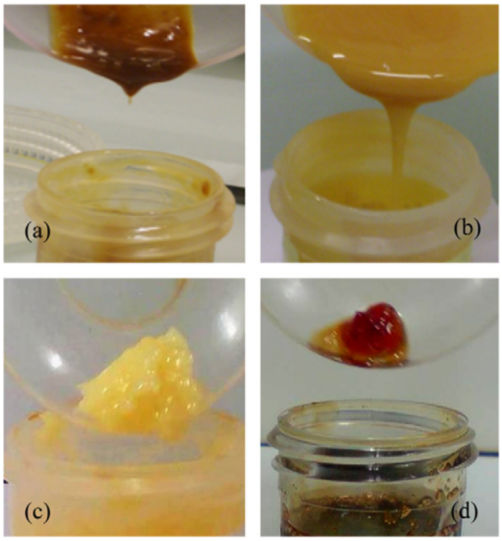

Fig. 4. Reconstitutions pictures: oils heated with litharge (20%wt of lead) without water (a) or with water (b). (c/d) are respectively a megilp according to Templeton's recipe and a Flemish medium.

3.2.3. And with spirit?

Before the 15th century, recipes often advised to place the varnish (made with oil probably treated with litharge and resins) in the sun to warm it to decrease its viscosity before spreading it with the hands on the painting [22]. We now know that diluting the mixture by adding spirits (also called essential oils) can overcome this difficult step. As an example, the viscosity of oil is 0.04 and that of turpentine is 0.0015 Pa s (Fig. 3b): thus adding turpentine decreases the viscosity without modifying the rheological behaviour. Turpentine is mainly composed of terpenes, obtained by distillation of pine resin. It dries by evaporation of the volatile part and its evaporation is quite slow and regular. It should also be noticed that turpentine when added to oil acts not only as a solvent but also accelerates the oxidation of oil by reacting with the oxygen of air [23]. That is why turpentine is an excellent solvent for vegetable oils and naturals resins.

It seems that spirits did exist and have been known for long but we do not very well understand why painters did not use them commonly to dilute varnishes. Some painters explain that Van Eyck obtained such optical effects because he superimposed a great number of glazes, made with thickened oil diluted with spirit. According to Helme and Rodde [24], the spirit may be spike oil (obtained from the distillation of lavender). Actually, this hypothesis cannot be verified as spirits evaporate. The commercial diffusion of spirits have grown up since the second part of the 15th century and one of the first indications of the use of turpentine (from the distillation of pine resin) is given by Leonardo da Vinci in the following advice: "To make oil good for painting: one part oil and one part turpentine (distilled once), and another part of twice distilled turpentine" [25].

With the growing use of spirits, painters also began to make the so-called spirit varnishes by solving resins no more in oils but in spirits. Fig. 5 illustrates the differences in the drying process of these two types of varnishes. The weight of the oil varnish increases after the application as oxygen is absorbed (Fig. 5a) whereas for spirit varnish the evaporation leads to weight loss (Fig. 5b). The range of order of the drying times involved is clearly different. The drying of spirit varnishes governed by the evaporation of the spirit is much faster than the one of oil varnishes. Concerning the flow properties of these mixtures of spirit and resin, they are also Newtonian, as mixtures of oil and spirit, and ternary mixtures of oil, resin and spirit.

4. Evolution of the oil painting medium: towards a 'perfect material'?

During the Renaissance period, the main required rheological properties were the same: a perfect finish without any brushstrokes. The medium used by Leonardo da Vinci for example allowed a perfect levelling (Fig. 6a). As seen in Section 2.2. flow out of the applied film is facilitated by low viscosity (under 0.2–0.3 Pa s at low shear rates), and by low or zero-yield value. This implies that the medium used by such painters had a low content of resin (under

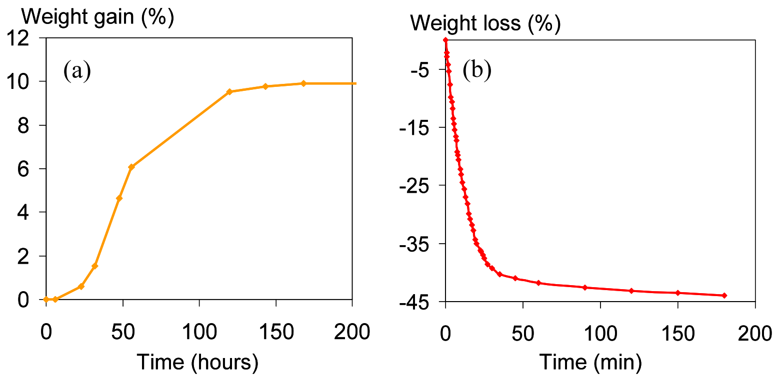

Fig. 5. Evolution of the weight of two varnishes after application: (a) is an oil varnish made with 37%wt of mastic resin and linseed oil. (b) is a spirit varnish containing 37%wt of mastic resin and turpentine. Around 0.06 g of each one is laid down on a glass substrate (2 × 6 cm) at ambient temperature.

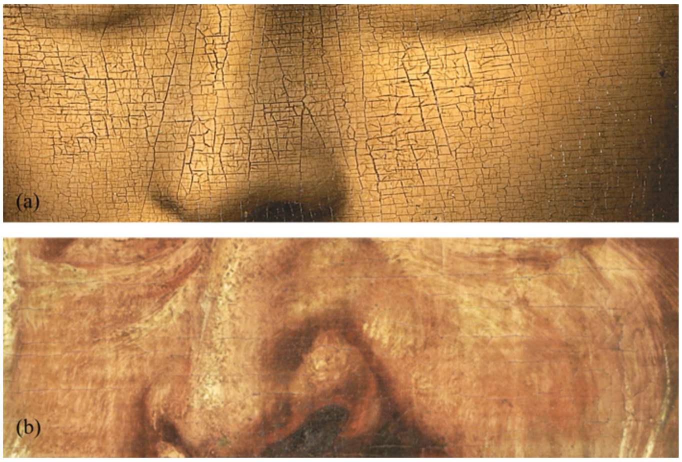

Fig. 6. Details of carnations from the *Gioconda* by Leonardo da Vinci (a), and an *Old man Portrait*, copied from Rubens (b).

25%wt), and/or lead oxide (under 20%wt) [18]. Moreover if resin was added to oil prepared with lead oxide, mastic resin could not be used as we will see later (formation of the so-called ‘Flemish medium’).

The main changes concerned the glaze technique in itself, which has been gradually modified by painters to paint faster. At the beginning, coloured glazes were applied on a white layer for the whole painting. To apply each layer of glaze, it was necessary to wait until the previous layer dries, at least two days for thin glaze layers. This can partly explain why glazes were gradually replaced by opaque layers. Leonardo da Vinci only applied glazes on opaque coloured layers to create the shadows with volume and depth. Then Venitian painters, following Titian (Fig. 2), superimposed dark and clear tones in thicker opaque layers and replaced the white preparation layer by bistre preparations more or less coloured [24].

A great change in the visual aspect of the painting can be noted with Rubens’ paintings (Fig. 2) at the beginning of the 17th century. The brushstrokes are now visible and are used by the painter to express movement and feelings (Fig. 6b). According to Maroger [12], Peter Paul Rubens used the “most facile and versatile vehicle that any painter has ever had at his disposal”. This so-called ‘Rubens medium’ was “a little more than a spoonful of the black oil (around 10%wt of PbO) with an even spoonful of mastic varnish”. Maroger explains that this mixture of oil boiled with litharge and resin mastic in certain proportions has the property to form a matter like a jelly. This medium, with which Rubens would have painted ‘la Kermesse’ in 24 hours [26], is still used by painters nowadays and sold as ‘the Flemish medium’. It would compile all the properties required for art painting: to be easily spreadable, to be fixed in order to be easily covered but to dry slowly in order to be modified easily. A certain force is necessary to apply it and after the application it thickens without drying. The artist can thus superimpose a new layer without mixing, or mix

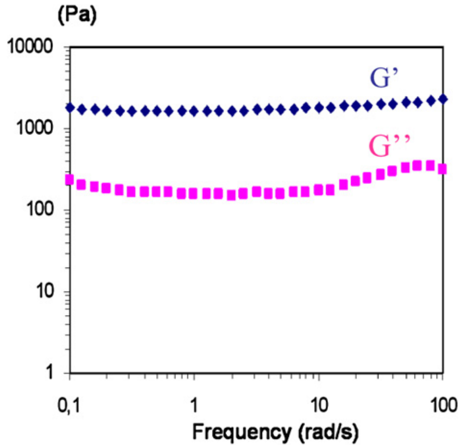

Fig. 7. Viscoelastic properties of a megilp: G' (◆) the elastic modulus, and G'' (■) the viscous modulus. This megilp was prepared following the Templeton's recipe, described in Section 3.1.1.

another colour with the previous one directly on the painting if a force higher than the yield point of the underlayer is applied.

The use of this medium by Rubens is only an assumption but it has to be noted that this kind of so-called jelly medium is very close to those used then by British 19th century painters like J.M. William Turner (Fig. 2). Indeed they commonly used 'megilps' or 'gumtions' described in the literature as home-made thixotropic oil/resin mixtures [13,27]. They are obtained by adding a basic lead compound to the ternary system linseed oil/mastic resin/turpentine. The main difference with the Rubens medium is the way lead is introduced in the mixture: in the Rubens medium, oil is heated with litharge, whereas for megilps lead acetate was commonly used (sugar of lead). As the Flemish medium, megilps are said to be an attractive medium for art paintings with excellent working qualities.

Reconstitutions were made and allow us to be a little more precise in the description of these medium (Figs. 4c and 4d). The preparation obtained according to the recipe of Flemish medium is black (Fig. 4d) but it can also be made with oil heated with litharge and water, which allow us to obtain a clearer medium. It is clearly shear thinning, with a high yield point and its value depends on the resin content. However it cannot be properly called a jelly as after mixing, the preparation flows with a rather low viscosity. The 'megilp' prepared according to Templeton's recipe corresponds more to a real 'jelly': it has strong elastic properties as seen in Fig. 7. Indeed the dynamical measurements performed showed that the elastic modulus G' is rather constant over the range of frequencies investigated and much higher than the viscous modulus G''. If shearing is applied (with a shear stress above 40 Pa, approximate value of the yield stress), it flows, and the flow properties are time and shear rate dependant. However, here again, the delay in the viscosity recovery is quite long and could not be observed in our experiments.

Such preparations must have interested the coatings industry as F. Kauer [9] indicates in 1960 that it has been possible since few years to gelify siccatives oils and to make them thixotropic by mixing with metals alginates.

5. Conclusion

Describing flow behaviours of ancient paint recipes and linking them to finish aspect of the paintings was thus possible. From Newtonian systems used at the Renaissance which allow to level any brushstroke, artists turned gradually to systems with more complex flow behaviours to create paste effects and express movements or feelings. As in research of paint industry, experimentations allowed the artists to prepare and use thixotropic, pseudoplastic or even gelly mixtures. Similar approach and techniques can be used in both domains, art paint and coating industry. Rheological characterization following the procedure introduced in coating industry would avoid any confusion in art paint description. However, defining in a general way a 'perfect' art paint formulation may seem restrictive: whereas in industry, the properties required and the corresponding rheological criteria are now quite well defined according to the application, in art and creation, everything can be done.

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