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Thermal analysis of the interaction of inorganic pigments with p(nBA/MMA) acrylic emulsion before and after UV ageing

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Corresponding Author:	Valentina Pintus AUSTRIA
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	
Corresponding Author's Secondary Institution:	
First Author:	Valentina Pintus
First Author Secondary Information:	
Order of Authors:	Valentina Pintus
	Rebecca Ploeger
	Oscar Chiantore
	Shuya Wei
	Manfred Schreiner
Order of Authors Secondary Information:	
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Response to Reviewers:	General comments: The minor remarks by the referee 2 are very much appreciated and they helped us to improve much more the quality of this paper. We have carefully considered all three minor comments and have tried to reply in a precise way. We have especially homogenized the figures and tables according to the requirements of the Journal. Referee 2: 1- Introduction. After lines 19-20 pag.3, use the forms "TG" or "DSC" instead of using

	entire names. Accepted. We have used the TG and DSC forms instead the entire names. 2- Experimental: page 5, lines 5-6: please specicy that 31 and 83 are related to UV ageing and add a note related to the choice of these time periods. Accepted. We have specified that 31 and 83 days correspond to the UV ageing and additionally we have explained the reason of the choice of these ageing periods adding the reference number 39 [ASTM International D2565 – 99 (Reapproved 2008) Standard Practice for Xenon-Arc Exposure of Plastics Intended for Outdoor Applications], which is related to that explanation. 3- page 9, line 55: there is a come before the full stop to be erased. Accepted. The coma has been erased. 4- Technical notes: Please use only black fonts in the text; the publisher will prepare the page-proof as it is. Accepted. We have provided all text using only black fonts. 5- The exotherm and/or endotherm directions should be marked in figures demonstrating calorimetric results. Accepted. The exotherm direction in the Fig 1 has been marked. 6- Please homogenize the titles of axes in all figures and table headings according to the standards of the Journal. (Example: Temperature/°C; Temperature/K; Mass/%; Heat flow/mW; Heat capacity/J g-1K-1 Time/min; Theta/degree; Wavenumber/cm-1 etc.). Accepted. We have homogenized the title of axes in all figures and table headings according to the standards of the journal. 7- Please use additional symbols for the designation in the figures. Please take it into consideration that the printed version of the Journal is black and white. Accepted. We have provided the figure 1 as well as 3, 4, and 5 in black and white form using different symbols.

Supplementary Material

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Revision notes on the reviews of the manuscript

Pintus V, Ploeger R, Chiantore O, Wei S, Schreiner M: Thermal analysis of the interaction of inorganic pigments with p(*n*BA/MMA) acrylic emulsion before and after UV ageing

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Thermal analysis of the interaction of inorganic pigments with p(*n*BA/MMA) acrylic emulsion before and after UV ageing

Valentina Pintus[1,2], Rebecca Ploeger[3], Oscar Chiantore[4], Shuya Wei[1], Manfred Schreiner[1,2]

1. Institute of Science and Technology in Art, Academy of Fine Arts, Schillerplatz 3, A-1010 Vienna, Austria
2. Institute of Chemical Technologies and Analytics, Analytical Chemistry Division, Vienna University of Technology, Getreidemarkt 9/161, A-1060 Vienna, Austria
3. National Gallery of Art, Washington DC USA
4. Department of Chemistry and Nanostructured Interfaces and Surfaces-Centre of Excellence, University of Torino, Via Pietro Giuria 7, 10125 Torino, Italy

v.pintus@akbild.ac.at
Tel.: +43 1 58816 8680, Fax: +43 1 58816 8699

Abstract

Differential scanning calorimetryic (DSC) and thermoal gravimetryic (TG) analseis were used to investigate the influence of inorganic pigments on the photo-oxidative stability of an acrylic emulsion binding medium. For this purpose, three different types of inorganic pigments such as ultramarine blue, cadmium red, and hydrated chromium oxide green were selected and mixed with an acrylic emulsion binding medium of poly(*n*-butyl acrylate/methyl methacrylate), p(*n*BA/MMA). These laboratory mixed paints were analysed before and after UV exposure for different periods of time. Additionally, three acrylic commercial paints such as ultramarine blue, cadmium red, and chromium oxide green from Liquitex® and Rembrandt® companies were also analysed. The results obtained with both thermal techniques suggested that ultramarine blue has the strongest influence on the photo-oxidative stability of the binding medium. A higher increase of the glass transition temperature T_g was observed by DSC analysis on the UV aged binder mixed with ultramarine blue. This result was confirmed by the TG investigations that showed a gradual decrease of the initial temperature of degradation as well as a strongest decrease of the final weightmass percent of the organic compounds. Similar results were measured from the Liquitex® and Rembrandt® blue paints.

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Keywords

Acrylic emulsion; inorganic pigments; ultramarine blue; UV ageing; DSC; TG;

1. Introduction

The composition of acrylic emulsion paints are particularly complex and their exact chemical compositions are kept a corporate secret by the paint manufacturers. In general, they are mainly a mixture of an acrylic emulsion as a binder, a pigment, and an extender (or filler). Through time the chemical and physical properties of the acrylic paint formulations have been improved using several chemically different additives. Depending on their type, additives are able to modify the colour, to improve the performance, to give resistance to heat degradation, and also to increase resistance to light degradation [1]. Particularly the pigments can influence the chemical stability of the acrylic binding media and they themselves can also be considered as additives. ~~The main commercially available white pigments are titanium dioxide (TiO_2), zinc oxide (ZnO), zinc sulphide (ZnS), and lithopone (a mixture of ZnS and $BaSO_4$). TiO_2 due to its whiteness and brightness because of its high refractive index and its relatively low and uniform absorption of visible light, is the most commonly used white pigment [2, 3] and it is also the main studied pigment [4, 5]. Spathis et al. [4] studied the photo-degradation of a series of Paraloid B72 films containing titanium dioxide (TiO_2) pigments. For this purpose, two crystallographic different kinds of TiO_2, anatase and anatase/rutile mixtures, were used in different concentration. The results obtained by Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography, and solubility measurements demonstrated that the presence of anatase pigment significantly improved the photo-stability of Paraloid B72 films [4]. In contrast, it has also been reported that anatase can form radicals and may degrade the polymers due to its high reactivity to ultraviolet (UV) radiation [6].~~

Among the coloured inorganic pigments, ultramarine blue, cadmium red and chromium oxide green are widely used in the acrylic emulsion paints. In particular, ultramarine blue pigment has a long history stretching back to ancient Egypt where the blue mineral lazurite was ground into a powder [~~7~~2]. Ultramarine blue pigment is a sodium aluminium sulfosilicate with a generally accepted empirical formula ($Na_6Al_6Si_6O_{24}S_4$) [~~8~~3]. The S_3^-, S_2^- radical anions and S_4 or S_3Cl are placed inside a sodalite framework (also known as the “β-cage”) with the generic formula $(Al_3Si_3O_{12})^{3-}$ and they are responsible for the colours of the ultramarine pigment [~~9~~4]. Inside the cage the Na^+ cations balance the

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negative charges [105]. The S_3^- radical anions are mainly responsible for the blue colour of the pigment. ~~It was demonstrated by using Raman spectroscopy that a higher amount of S_3^- chromophore with small amount of S_2^{--} – responsible for the yellow colour [11] – was present in the blue ultramarine than in the violet ultramarine, which contained an higher amount of the red chromophores (S_4 or S_3Cl) [12]. Furthermore,~~ Del Federico et al. [126] investigated the fading of the blue ultramarine pigments in simulated fresco environments, which corresponded mainly to the decrease of the major S_3^- chromophores. Generally, ultramarine blue has a good lightfastness and heat stability (>350 °C) [83], but a low resistance to acids resulting in the conversion of the free chromophores into H_2S and possibly elemental sulfur [126]. The ultramarine pigment exhibited a low UV absorption and small protective effect on the UV stability of unstabilized polypropylene [137]. However, the absorption alone is not the only contributing influence on the UV stabilisation because the chemical and physical properties of the pigment may also control the stabilisation of a polymer [148]. Additionally, a comparably low photo-oxidative stability of ultramarine blue commercial acrylic paints was shown by colour measurements, Py-GC/MS and FTIR-ATR analys~~i~~es [159].

Compared to ultramarine blue, cadmium red is regarded as one of the most stable pigments with a good hiding power, moderate tinting strength and good thermal stability [1610]; however, it can oxidize to cadmium sulphate when exposed to light in presence of moisture, leading to a consequent loss in colour intensity [72]. Generally, cadmium red is considered a good stabilizer [1711] and it is especially more stable to bleaching when exposed to UV light and air than cadmium yellow, which can oxidise into insoluble colourless sulphates [1812] mainly due to the added zinc [1610]. Cadmium red is based on cadmium sulfide and sulfoselenide (CdS, xCdSe) and is a product of a reaction between cadmium and sulphur resulting with a hexagonal wurtzite lattice crystallization form. The addition of the selenium in the intercrystalline lattice contributes to the darkening of the red colour, up to a maximum useful cadmium selenide content of 50 mole percent [1812, 1913]. Although cadmium red acrylic paints are widely formulated by the artist paint companies, its use is prohibited in many countries because of the toxicity of the soluble cadmium [72].

Chromium oxide green pigment – also known as chromium sesquioxide – is characterized by chromium(III) oxide, (Cr_2O_3), with an eskolaite mineral form and with a dark olive-green shade. It is listed by the *Colour Index* (1971) as CI 77288/Pigment

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Green 17 (PG17). It is often confused with chrome green and fast green pigments, which are a blend of chromium yellow and iron blue or phthalocyanine pigments [~~18~~12]; mixtures can provide a colour range from light yellow green when the percentage of iron blue is very low, to a dark green colour by increasing the percentage of iron blue [~~20~~14]. Additionally, there is a hydrated form - hydrated chromium sesquioxide ($Cr_2O(OH_4)$) - listed as *Colour Index* CI 77289/Pigment Green 18 (PG18) and also called Viridian (from Latin *Viridis*: green). The chromic oxides pigments are thermally stable and insoluble in water [~~18~~12] and they are considered to provide good UV stabilization for polyolefins [~~21~~15]. Unlike chromium oxide green, the thermal stability of Viridian pigment is low because it starts to loose its water content at 95°C [~~7~~2].

All of these three inorganic pigments have a critical influence on the photo-stability of an acrylic emulsion binding medium when exposed to UV light. Consequently, UV light has an important effect on the photo-oxidative stability of modern and contemporary works of art based on acrylic emulsions, especially those exposed in outdoor conditions, compared to those kept in indoor conditions such as museums or private collections. In particular, the UV-B light (315 to 280 nm, middle UV) may cause discoloration, cracks, and other damages on acrylic materials placed in external environments [~~22~~16]. Several UV ageing studies have been carried out on the co-emulsion of poly(*n*-butyl acrylate/methyl methacrylate), p(*n*BA/MMA), in order to investigate the long-term effects on the physical and optical properties, especially considering wavelengths between 400 and 315 nm (UV-A, near UV), which are normally present in indoor conditions, [~~23~~17-~~25~~19]. Since the late 1980s, most artists acrylic emulsion paints are based on a p(*n*BA/MMA) emulsion binding medium, which ~~shows a superior hydrophobicity in comparison with poly(ethyl acrylate/methyl methacrylate), p(EA/MMA). They~~ have been adopted and used by many paint companies [~~26~~20]. It has been demonstrated that wavelengths in the UV region can cause chemical reactions in the polymer structure such as chain-breaking and cross-linking with the decomposition of the synthetic material [17]. ~~It has been demonstrated that wavelengths in the UV region can cause chemical reactions in the polymer structure such as chain-breaking and cross-linking with the decomposition of the synthetic material [23]. Scalarone et al. [25] demonstrated by colour measurements that p(nBA/MMA) and p(EA/MMA) co-polymers have a high resistance to yellowing. Additionally, a decreased solubility of all p(nBA/MMA) copolymer paint samples in comparison with p(EA/MMA) copolymer paints was determined. Chiantore et al. [27] used a Xenon light source filtered for λ<295 nm to investigate acrylic~~

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~~polymers characterized by long ester groups, such as *n*-butyl groups, and observed a fast and extensive cross-linking in combination with some fragmentation, due to the favored oxidation on the tertiary carbon of the butyl group. In addition, some attention has been paid to the competition between chain scission reactions and cross-linking reactions during the photo-oxidative degradation, which is mainly controlled by the glass transition temperature T_g of the polymer. Polymer chains above their T_g*s* (surface glass temperature transition) would preferentially undergo cross-linking [28]. Additionally, the development of cross linking in two commercial acrylic dispersions – BA/MMA and EA/MMA formulations – after accelerated photo-ageing was directly related to the progressive reduction of ultimate tensile strengths, although the moderate increase of the T_g values studied by differential scanning calorimetry (DSC) remains in an acceptable range of use [29].~~

DSC and ~~thermal gravimetry (~~TG~~)~~ analyses have been widely used in the field of art [21-24] and ~~analysis~~ represent two valuable techniques for the study of the thermal properties of acrylic emulsion materials. The determination of the glass transition temperature (T_g) by differential scanning calorimetry (DSC) is a useful method to define the state of an acrylic material at room temperature. Below the T_g the material is usually in a glassy and hard state and above the T_g is normally in a soft and rubbery state. Thus a change of the T_g, possibly due to the addition of a pigment or to the UV ageing, can indicate whether the material becomes more brittle and fragile (increase of the T_g) or more tacky and soft (decrease of the T_g). Additionally, DSC has been applied for the investigation of paint media in order to analyze the influences of the pigment and of the binding medium based on the shape of the thermal analysis curve [25].

The thermogravimetry (TG) analyses carried out under an inert atmosphere and non-isothermal mode have commonly been applied to understand the thermal degradation behaviour and the challenging composition of different modern synthetic materials used in the field of modern and contemporary art [18, 19, 26-29]. The organic component of acrylic paints, mainly based on the acrylic binding medium, usually decomposes in a range of temperature between 300 and 500 °C [30], where also several additives might thermally react. In contrast, the inorganic part, consisting of inorganic pigments and/or different fillers is quite stable at high temperature, although some decomposition reactions may occur depending on their type and origin. Furthermore, ~~T~~the thermo~~al~~ gravimetr~~y~~ic ~~(TG)~~ technique was also used to determine the amount of different organic components in several pigmented artists´ acrylic emulsions under different ageing

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conditions [3026]. ~~DSC has been applied for the investigation of paint media in order to analyze the influences of the pigment and of the binding medium based on the shape of the thermal analysis curve [31].~~

So far, pigmented and un-pigmented modern acrylic materials have been characterized and identified [~~15~~9, ~~22~~16, ~~30~~26, ~~32~~31-~~38~~37], but detailed data on the influence of inorganic pigments on the stability of acrylic emulsion paint films are still lacking. As UV ageing studies of unpigmented synthetic binding media does not accurately reflect the UV ageing of synthetic paints because of all other components present that can also contribute significantly to their degradation under UV, the exact context of the degradation still remained unclear in many cases. Therefore, more studies concerning the influence of inorganic pigments on acrylic emulsions are desirable. Especially, the influence of UV-B light on the stability/degradation of materials in works of art in outdoor environments has been rarely investigated. Pintus et al. [~~22~~16] studied the influence of UV-B light on pure acrylic emulsions as well as their mixture with different inorganic pigments showing material alterations and the formation of new products, which were recorded by FTIR-ATR. Generally, these changes were more pronounced when the acrylic binding media were mixed with pigments. Moreover, similar results w~~h~~ere observed for different acrylic commercial paints [~~15~~9]. Dimers, trimers and sesquimers were already detected at lower temperatures (<300°C) by Py-GC/MS double-shot technique, which demonstrated the important UV impact on the thermal stability of the acrylic paints [~~15~~9, ~~22~~16].

Based on these previous studies [~~15~~9, ~~22~~16], the influence of three different inorganic pigments, ultramarine blue, cadmium red, and hydrated chromium oxide green, on the stability of a co-p(*n*BA/MMA) acrylic emulsion when exposed to the UV light, was investigated by differential scanning calorimetry~~ic~~ (DSC) and therm~~o~~al ~~-~~gravimetry~~ic~~ (TG) analys~~ic~~s on the prepared samples before and after UV exposure. Both thermal techniques are fundamental for studying the thermal stability and ~~behavior~~behaviour of a polymeric material. In particular, a change of the glass transition temperature in an acrylic emulsion film is considered as an indicator of photo-oxidative degradation [~~29~~38]. Additionally, the above mentioned colours of two different commercial companies (Liquitex® and Rembrandt®), which were previously characterized by Py-GC/MS as a co-p(*n*BA/MMA) acrylic emulsions binding medium [~~15~~9], were selected for a comparison with the self-made samples. Unfortunately, it was not possible to find the hydrated

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chromium oxide green paints based on a co-p(*n*BA/MMA) acrylic binder. The objective of this study is to investigate the influence of three widely used inorganic pigments on the photo-oxidative stability of a well-known p(*n*BA/MMA) acrylic emulsion.

2. Experimental

To evaluate the influence of three inorganic pigments on the photo-oxidative stability of a p(*n*BA/MMA) acrylic emulsion binding medium, each specimen (Table 1) was analyzed by differential scanning calorimetry (DSC) and thermogravimetry (TG) analyses before and after UV exposure, respectively 31 and 83 days of UV ageing. According to the ASTM 2565 – 99 standard [39], the exposure time of the specimens under UV light was established from a long-term evaluation and control of the material. This evaluation was periodically carried out under an optical microscope – to observe any change in the morphology of the surface – and by Fourier transform attenuated total reflection (FTIR-ATR) analysis. 31 and 83 days of UV ageing were then chosen, because of noticeable changes.

Due to the need of a relatively high amount of sample material for DSC and TG analyses, it was not possible to investigate the pure acrylic binding medium Plextol® D498 after 31 and 83 days of UV ageing. By lightly scraping the paint film from the glass slide with the help of a scalpel, a higher brittleness and a decreased plasticity were observed, which could be considered as an effect of the photo-oxidative ageing.

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2.1 Sample preparation

Approximately 60 mg of a pure acrylic binding medium (Plextol® D498) was cast separately on glass plates, which produced a dried film with a thickness in a range of 10-20 µm. Additionally, different mock-ups of pure Plextol® D498 mixed with inorganic pigments such as ultramarine blue, cadmium red, and hydrated chrome oxide green in a mixing ratio of about 3:1 were cast on glass plates. The dried film thickness of these paint samples was approximately in the range of 30-40 µm. The acrylic emulsions binding medium and the inorganic pigments were products of KREMER (Kremer Pigmente Gmbh & Co. KG, Germany). Moreover, approximately 200 mg of three acrylic paint colours (ultramarine blue, cadmium red, and chromium oxide green) from 2 companies (Liquitex® and Rembrandt®) were also cast on glass plates, producing a dried film with an average thickness of 130 µm. In total, 12 identical specimens for the pure acrylic binding medium, three for each pigment mixed with an acrylic emulsion, as well

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as three for each commercial acrylic paint colour were made, in order to obtain a sufficient number of samples for the tests in the UV chamber. After drying for 24 h at room temperature (pure acrylic binding media and mixed with pigments) and for 3 months at room temperature (commercial acrylic paint colours), the glass plates were arranged in the UV chamber, except for the standard samples representing the unaged compositions. The commercial acrylic paints were left to dry for a longer period of time in comparison to the pure and mixed acrylic binding media due to their higher film thickness which required longer drying time [~~39~~40].

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2.2 UV exposure

UV exposure of the samples was carried out in a UV chamber, UVACUBE SOL 2/400F, produced by Dr. Hönle GmbH UV-Technology, Germany. The UV light radiation source was supplied by a 910 W/m^2 Xenon arc solar simulator with an incorporated H2 filter, which provides radiation with wavelengths between 295 nm and 800 nm. The chamber temperature was 48.8 °C. No control of the relative humidity (RH) was possible in the UV exposure chamber used, therefore the RH varied between 30 and 35% depending on the RH in the ambient atmosphere. Samples were aged for 31 and 83 days, respectively.

2.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry~~ic~~ analyses were performed with a DSC Q200 instrument (TA Instruments – Waters LLC Lukens Drive New Castle, DE 19720). Approximately 7 mg of the sample material were scraped from each glass slide for the analysis. The differential scanning calorimetry~~ic~~ (DSC) analyses were performed at a heating rate of 20 °C/min from -10 °C (held for 2 min) to 150 °C (held for 2 min), then cooled to -10 °C (held for 2 min) at a heating rate of 20 °C/min and repeated for a second time under a nitrogen air flow of 50 mL/min. TA Universal Analysis software (TA Instruments, USA) was used for visualising the results. The inflection point was considered for the calculation of the T_g using the TA program. The T_g was taken at the second heating cycle.

2.4 Thermo~~gal G~~ravimetry (TG)

Thermo~~al~~ gravimetry~~ic~~ analyses were performed with a TGA Q500 instrument (TA Instruments – Waters LLC Lukens Drive New Castle, DE 19720). The TG instrument

was equipped with an autosampler and an ultra-sensitive thermo balance. The nitrogen gas flow was set at 40 mL/min for the tare and at 60 mL/min for the samples analyses. The visualisation of the results was performed with the Universal Analysis software (TA Instruments, USA). For the analysei~~s~~ approximately ~~15~~ 12 mg of sample material were scraped for each glass slide. Therm~~o~~al ~~-~~gravimetry~~ic~~ analyses were carried out at a heating rate of 10 °C/min from 30 °C ~~up~~ to 800 °C.

3. Results and Discussion

~~To evaluate the influence of three inorganic pigments on the photo-oxidative stability of a p(*n*BA/MMA) acrylic emulsion binding medium, each specimen (Table 1) was analyzed by differential scanning calorimetry (DSC) and thermal gravimetry (TG) analysis before and after UV exposure, respectively 31 and 83 days. Due to the need of a relatively high amount of sample material for DSC and TG analysis, it was not possible to investigate the pure acrylic binding medium Plextol® D498 after 31 and 83 days of UV ageing. By lightly scraping the paint film from the glass slide with the help of a scalpel, a higher brittleness and a decreased plasticity were observed, which could be considered as an effect of the photo-oxidative ageing.~~

3.1 Differential Scanning Calorimetry~~ic analysis~~ (DSC) results

~~The determination of the glass transition temperature (T_g) by differential scanning calorimetry (DSC) is a useful method to define the state of an acrylic material at room temperature. Below the T_g the material is usually in a glassy and hard state and above the T_g is normally in a soft and rubbery state. Thus a change of the T_g, possibly due to the addition of a pigment or to the UV ageing, can indicate whether the material becomes more brittle and fragile (increase of the T_g) or more tacky and soft (decrease of the T_g).~~ DSC analysis of the unaged mock-ups indicated two material properties: 1) The glass transition temperature T_g and 2) the melting temperature T_m of the surfactant. All values are reported in Table 2. The pure acrylic binding medium as well as its mixture with pigments shows the T_g around 10 °C. These results suggest that the addition of pigments does not influence the T_g of the paint films extensively, which corresponds to a value generally near or below room temperature. The low influence probably results from the weak interaction between the pigments and the acrylic binder [~~40~~41]. The T_g endothermic signal of the Plextol® D498 binding medium was followed by a peak at around 55 °C. The detection of this peak corresponds to the melting temperature T_m of

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the surfactant, previously identified as a polyethoxylated ~~PEO~~ based non-ionic surfactant [~~22~~16]. The surfactant is an important component in the acrylic emulsions, ~~mainly~~ used to obtain a stable dispersion of the polymer particles in the water~~lower the interfacial tension between the monomer and the water~~ [~~. 22~~].

In contrast to these results from the pure acrylic material, the DSC curve of the acrylic binding medium when mixed with hydrated chromium oxide green did not show any endothermic peak. The interaction of the green pigment with the binding medium probably caused an early exudation stage of the surfactant from the matrix to the surface with a successive degradation or volatilization reactions. It is well known that the non-ionic surfactants have the tendency to migrate towards the surface of the acrylic emulsion paint films, causing changes in gloss and surface roughness [~~41~~42], and which may undergo total degradation under UV exposure [~~15~~9, ~~22~~16, ~~42~~43]. It has to be stressed that the mock-ups were prepared only with a mixture of the acrylic emulsion binding medium with the inorganic pigment. No other components were added, although there probably would be additives in industrial products. ~~that~~ These additives could possibly improve the ~~stabilization~~ stability of the chemical system ~~which are probably used in industrial products.~~

Depending on the type of pigment mixed with the acrylic binding medium some different ~~behaviors~~behaviours could be noticed concerning the UV aged samples. In particular, the ultramarine blue pigment affected the photo-oxidative stability of the binding medium more than the other pigments. After UV ageing for 31 and 83 days the T_g increased by more than 7 °C, when the binder was mixed with the ultramarine blue pigment (Table 2). This is possibly related to cross-linking in the polymer network during the photo-oxidative ageing, which influences the motion of the segment chains in the macromolecules [~~29~~38]. On the other hand, the loss of organic material by the evaporation of low molecular ~~weight~~mass degradation products that would otherwise act as plasticizing agents, with a consequent increase of the T_g into the paint film [~~43~~27] could also take place. Normally, the soluble fraction of the acrylic emulsion decreases in molecular ~~weight (MW)~~mass during UV ageing [~~24~~18] by the loss of volatile scission products and other molecules that can evaporate or be lost. The loss of molecules is most ~~probable~~ probably due to the formation of low molecular ~~weight~~mass molecules such as unspecific aldehyde, lactones, and acidic oxidation products found in these acrylic emulsions paints and demonstrated in the previous study by FTIR-ATR spectroscopy [~~22~~16]. Independently from the type of inorganic pigment, the endothermic

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peak of the non-ionic surfactant totally disappeared after 31 and 83 days of UV ageing in all mock-ups, corresponding to the total loss of the surfactant in the acrylic material due to the photo-ageing reactions in accordance to a previous work [~~22~~16].

The comparison of the unaged and aged mock-ups with the unaged and aged commercial acrylic colours shows different ~~behaviors~~behaviours. Unlike the mock-ups, all unaged commercial acrylic paints showed two broad transitions, an exothermic one in the temperature range of approximately 0-50 °C, ~~-~~and one endothermic between 50-100 °C shown as example in Figure 1 for Liquitex® Blue. The initial broad exothermic transition affects the measurement and evaluation of the T_g that is related with a small change in heat capacity. This may be due to the interaction between organic and inorganic components in the paint film since most of the analyzed paints contain inorganic fillers (Table 1). These latter and especially nanofillers are known to interact strongly with the polymer forming an inter-phase region [~~40~~41]. Their interaction restricts the polymer chains mobility [~~40~~41] with a consequent complexity in the determination of the T_g. The diffuse endothermic process might be correlated to the loss of volatile components such as absorbed water.

In all unaged Liquitex® colours the T_m of the surfactant – previously identified as the PEO based non-ionic surfactant [~~1~~59] – was detected in the first heat cycle at around 43 °C and accompanied at lower temperature (38 °C) by another endothermic peak with a smaller area (Fig. 1). This double-melting ~~behavior~~behaviour of the non-ionic surfactant may be due to a preliminary melting at low temperature of minor crystals. Double-melting peaks have been observed during a DSC analysis in many semicrystalline polymers [~~44~~44]. They are normally attributed to the melting of imperfect crystals formed during the annealing stage and their recrystallization [~~44~~44]. Furthermore, the presence of a poly(acrylic) type thickener or an anionic surfactant [~~1~~59] which is used with non-ionic PEO surfactants to improve the electrostatic stabilization of the inorganic pigment in the emulsion [~~37~~36, ~~44~~45], likely also influences the melting point of the surfactant. The increase in the amount of the PEO surfactant in a non-ionic/anionic blend (PEO/Carbopol) with the subsequent variation of the melting peak of the PEO observed in the DSC curve has been reported [~~46~~46].

In contrast to these results, the DSC curves of all Rembrandt® colours do not show any surfactant melting peak, likely because of their very low concentration. The melting peak of the surfactant might also vary depending on the amount of the pigment added in the paint. For instance, Hagan et al. [~~47~~28] demonstrated by DSC analysis that the

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magnitude of the melting peak of the surfactant in a latex paint film diminishes in area by increasing of the amount of TiO_2 in the mixture, suggesting that the pigment affects the structure of the surfactant within the film.

By comparing the obtained results of the unaged and aged commercial acrylic paints after 31 and 83 days of UV exposure, a general increase of the T_g was observed in all acrylic paints. In particular~~ly~~, a significant increase in the T_g of almost 10 °C (see Table 2) was found in the Rembrandt® paints, which showed a lower stability in comparison to the Liquitex® colour paints. Similarly to the aged mock-ups, the increase in the T_g can be related either to a major network change in the polymer binder due to some cross linking reactions or to the evaporation of volatile degradation products. This alteration can possibly explain the brittle handling ~~behavior~~behaviour of the aged paint films.

Moreover, the UV ageing affected the stability of the non-ionic surfactant in all Liquitex® films in accordance to the results reported in a previous study [~~15~~9]. Similar to the mock-ups samples, the double melting peak was not visible anymore already after 31 days of UV ageing.

3.2 Thermo~~gal G~~ravimetry (TG) results

~~The thermal gravimetric analysis carried out under an inert atmosphere and non-isothermal mode have commonly been applied to understand the thermal degradation behavior and the challenging composition of different modern synthetic materials used in the field of modern and contemporary art [24, 25, 30, 43, 48, 49]. The organic component of acrylic paints, mainly based on the acrylic binding medium, usually decomposes in a range of temperature between 300 and 500 °C [50], where also several additives might thermally react. In contrast, the inorganic part, consisting of inorganic pigments and/or different fillers is quite stable at high temperature, although some decomposition reactions may occur depending on their type and origin.~~

The initial ~~and final~~ degradation temperature ~~(°C)~~ and the ~~weight~~mass percentages ~~(%)~~ of the final organic and ~~inorganic~~ residue components of the ~~analyzed~~ pure binding medium analyzed, its mixture with pigments and the commercial acrylic paints before and after 31 and 83 days of UV ageing, are summarized in Table 3. In addition the ~~weight~~mass loss percentage ~~(%)~~ of the organic components for each unaged and aged sample is shown in figure 2.

As it is reported in Table 3, the TG results of the unaged pure acrylic binding medium as well as its mixture with the inorganic pigments (Fig. 3a, 3b) are mainly characterized by

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a single step degradation process between approximately 300 °C and 440 °C. The ~~weight~~mass loss ~~(%)~~ at this step is mainly associated with the decomposition of the acrylic binder based on the co-polymer aqueous dispersion of poly(*n*-butyl acrylate/methyl methacrylate), p(*n*BA/MMA)~~, which is expected thermal degradation behavior of the acrylic polymers~~. Mostly monomers and oligomers are formed by the conversion of the macromolecular chains into volatile compounds at high temperatures [~~30~~26]. ~~For the unaged binding medium and its mixture with pigments it was possible to determine the final temperature of the single degradation process which was around 440 °C.~~ A small residue of about 8% of ~~weight~~mass and an initial degradation temperature at 299 °C were observed in the TG curve of the unaged binding medium.

In addition to the single step degradation process, the TG curve of the cadmium red film (Fig. 4) is characterized by a slight loss of ~~weight~~mass at approximately 750 °C; this is probably related to the decomposition of the cadmium selenide [~~51~~47].

The comparison between the results obtained for the unaged and UV aged mock-ups showed that the p(*n*BA/MMA) co-polymer is more sensitive to the photo-oxidative reactions when ultramarine blue is added into the matrix (Fig. 3a). ~~While the final degradation temperature in the TG curves of the ultramarine blue films remained basically the same, T~~the initial temperature of decomposition in the TG curves of the blue ultramarine films decreased after 83 days of UV exposure, dropping from 311 to 121 °C (Table 3). This change in the thermal stability is accompanied by a decrease of the final ~~weight~~mass percent of the organic component from approximately 64 to 45%, which can indicate a pronounced decomposition of the acrylic binding medium into volatile compounds through chain scission reactions during UV exposure and consequently loss of the volatile degradation species. The ultramarine blue pigment, which is known to decompose in aqueous solution and release sulfur species [~~52~~48], evidently reduced the thermal stability of the p(*n*BA/MMA) binder, acting as catalyst in the degradation of the paint film.

A different ~~behavior~~behaviour in the TG results was observed when the binder was mixed with the cadmium red pigment (Fig. 3b). The initial temperature of decomposition increased already after 31 days of UV ageing from 297 to 337 °C, instead of the decrease of the ultramarine blue film~~, and A~~after 83 days it remained basically the same. Some cross linking reactions could have taken place in the polymer material with a consequent reduced mobility of the macromolecular chains and retardation in the thermal degradation.

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In contrast to the TG results of the ultramarine blue ~~mixed with the acrylic emulsion~~ and the cadmium red film mixed with the acrylic emulsion, no relevant differences were detected when the acrylic binder was mixed together with the hydrated chromium oxide green pigment (Table 3).

The thermal degradation curves of the unaged commercial acrylic paints showed more transition steps during decomposition in comparison to the results obtained for the mock-ups. ~~, which~~ This is well confirmed by their derivate ~~weight~~mass loss data (Fig. 4a, 4b, 5a, 5b). These multiple transitions are mainly due to the complex chemical composition of the manufactured paints, which includes the addition of different extenders into the material (Table 1). For instance the TG curves of the Liquitex® and Rembrandt® blue and of the Liquitex® green are mainly characterized by two steps degradation patterns. Table 3 shows that the first step started below 90 °C up to 190 °C, associated with a ~~weight~~mass loss up to 2% in the Liquitex® (Fig. 4a) and Rembrandt® blue paint film (Fig. 4b) which could be attributed to the evaporation of loosely bound water. The second and main ~~weight~~mass loss was approximately between 300 to 440 °C, which corresponded to about 55%. This is caused by the decomposition of the co-polymer binder, similar to the TG results of the mock-ups. In addition to the two degradation steps, the Liquitex® and Rembrandt® red (Fig. 5a) films also showed a third minor step. This variation corresponded to a slight ~~weight~~mass loss of 4% at approximately 700 and 740 °C respectively, probably related to the decomposition of cadmium selenide (CdSe). Furthermore, the TG curve of Rembrandt® red (Fig. 5a) was characterized by the decomposition of calcium carbonate beginning at 600 °C on, which is commonly used as filler in acrylic paints and well known to decompose into carbon dioxide and calcium oxide at high temperatures [~~24~~18, ~~30~~26]. This is clearly visible in the derivative ~~weight~~mass loss curve with the formation of a small peak and complemented by another unknown peak around 700 °C possible related to additional filler (Fig. 5a). The TG curve of the Rembrandt® green (Fig. 5b), which was also characterized by the loss of carbon dioxide from the calcium carbonate filler, seemed to be quite complex. Besides the first two steps of water evaporation and of the polymer decomposition, an unclear gradual decay was additionally found at approximately 400 °C, which corresponded to 3% of ~~weight~~mass loss.

The TG results obtained from the UV aged commercial acrylic samples showed that the most pronounced effect of photo-oxidative reactions were in the ultramarine blue acrylics. For instance, the comparison of the TG curves of the unaged and aged

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Liquitex® blue paint films (Fig. 4a) showed three main differences: 1) after 31 days of UV ageing the decomposition started at lower temperature which further decreased after 83 days with a total temperature difference of 50 °C. Some chain scission reactions could have taken place in the co-polymer binder during the UV exposure, resulting in a reduced thermal stability. 2) The final ~~weight~~mass percent decrease of the organic part ~~decreased~~, corresponding to 5%, ~~which is~~is probably due to photo-oxidizing processes of the paint film and a loss of volatile molecules. 3) No trace of the loosely bounded water~~, previously found which was found~~ between 82 and 189 °C in the unaged sample, was detected~~, was detected~~. All of these three effects of the UV ageing on the paint film were more accentuated in the Rembrandt® blue (Fig. 4b), including even a decrease of 7% of the final organic part ~~of 7%~~. Additionally, a gradual increase of a new small transition step from 129 to 199 °C, which is related to the formation of an unassigned small peak in the derivative ~~weight~~mass loss curve, was observed in the aged Rembrandt® blue sample.

Unlike ultramarine blue paints, the cadmium red paint films from Liquitex® and Rembrandt® (Fig. 5a) seemed to be less sensitive to the UV light. No trace of the loosely bounded water was observed, and the TG curves of the unaged and aged cadmium red acrylic materials were characterized by a small increase of the initial temperature of decomposition as well as ~~only~~ a small ~~increase~~ decrease of the final ~~weight~~mass of the ~~in~~organic component. Similar to the cadmium red mock-up, some cross linking reactions between the molecular chains in the acrylic emulsion binding medium might have occurred, resulting in a consequent increased resistance of the material to high temperatures.

Concerning the green paints, the Liquitex® green showed a reduced stability based on the gradual decrease~~d~~ of the initial temperature of degradation (from 295 to 277 °C), as well as the decrease of 5 % on the final ~~weight~~mass percentage of the organic compound ~~of 5 %~~ (Table 3), similar to the ultramarine paints.

Conclusions

The influence of ultramarine blue, hydrated/chromium oxide green and cadmium red pigments on the stability of a p(*n*BA/MMA) acrylic binding medium when aged under UV exposure for 31 and 83 days was studied by differential scanning calorimetry (DSC) and thermo~~al~~ gravimetry (TG) analysi~~e~~s. Generally, a reduced photo-oxidative stability of the p(*n*BA/MMA) acrylic binder was observed when mixed with ultramarine blue, as well as

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for the Liquitex® and Rembrandt® blue paints containing p(*n*BA/MMA). The ultramarine blue pigment seemed to promote some chain scission reactions in the polymer matrix observed as the loss of organic material by the evaporation of volatile compounds. This was shown by DSC as an increase in the T_g of the paint films after 83 days of UV ageing, and further supported by the TG results which showed a decrease of the initial degradation temperature, and an associated decrease of the final ~~weight~~mass percentage of the organic compounds. A similar ~~behavior~~behaviour was shown by the chromium oxide green, especially by the Liquitex® green, while the hydrated chromium oxide green mixed with the p(*n*BA/MMA) acrylic binder remained basically stable.

In contrast to ultramarine blue and hydrated/chromium oxide green, the cadmium red pigment seemed to promote a greater amount of cross linking in the acrylic film network. This was indicated by the TG analysis that showed an increase of the initial degradation temperature, as well as by the DSC analysis that showed a gradual increase in the T_g temperatures. In these specimens not only the pigment can influence the photo-stability of the binding medium, but also the fillers and other additives so far not identified, may play an important role.

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Figure captions

Fig. 1 Differential scanning calorimetryic (DSC) curves of the of the Liquitex® blue paint containing p(*n*BA/MMA) before ageing (black solid lines) and after UV ageing for 31 (green pointed lines) and 83 (red dashed lines) days

Fig. 2 Weight Mass/% percentage (%) of the final organic components of each unaged and aged commercial acrylic paints obtained by thermoal gravimetry (TG) analysis. The ageing was carried out under UV exposure for 31 and 83 days, respectively

Fig. 3 Thermoal gravimetryic (TG) curves and their derivates weight mass/(%) of Plextol® D498 p(*n*BA/MMA) mixed with ultramarine blue **(a)** and mixed with cadmium red **(b)** before ageing (black solid line), and after UV ageing for 31 (green pointed line) and 83 (red dashed line) days

Fig. 4 Thermoal gravimetryic (TG) curves and their derivates weight mass/(%) of the Liquitex® blue paint containing p(*n*BA/MMA) **(a)** and of the Rembrandt® blue paint containing p(*n*BA/MMA) **(b)** before ageing (black solid line), and after UV ageing for 31 (green pointed line) and 83 (red dashed line) days

Fig. 5 Thermoal gravimetryic (TG) curves and their derivates weight mass/(%) of the Rembrandt® red paint containing p(*n*BA/MMA) **(a)** and of the Rembrandt® green paint containing p(*n*BA/MMA) **(b)** before ageing (black solid line), and after UV ageing for 31 (green pointed line) and 83 (red dashed line) days

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Sample	Colour	Pigment Classical Name	Chemical Composition	Colour Index: Generic Name
Plextol® D498 + ultramarine blue	Blue	Ultramarine blue	p(*n*BA/MMA) + $Na_8Al_6Si_6O_{24}.Sx$	PB 29
Plextol® D498 + hydrated chromium oxide green	Green	Hydrated chromium oxide green	p(*n*BA/MMA) + $Cr_2O_3 \cdot 2H_2O$	PG 18
Plextol® D498 + cadmium red	Red	Cadmium red medium	p(*n*BA/MMA) + CdS, xCdSe	PR 108
Liquitex® Professional Acrylic artist color, USA/Canada	Blue	Ultramarine blue	p(*n*BA/MMA) + $Na_8Al_6Si_6O_{24}.Sx$ + Kaolinite ($Al_2Si_2H4O_9$)	PB 29
Liquitex® Professional Acrylic artist color, Usa/Canada	Green	Chromium oxide green	p(*n*BA/MMA) + Cr_2O_3	PG 17
Liquitex® Professional Acrylic artist color, USA/Canada	Red	Cadmium red light	p(*n*BA/MMA) + CdS, xCdSe	PR 108
Rembrandt® Artists Quality Extra Fine, Holland	Blue	Ultramarine blue	p(*n*BA/MMA) + $Na_8Al_6Si_6O_{24}.Sx$ + Kaolinite ($Al_2Si_2H_4O_9$)	PB 29
Rembrandt® Artists Quality Extra Fine, Holland	Green	Chromium oxide green	p(*n*BA/MMA) + Cr_2O_3 + Calcite ($CaCO_3$)	PG 17
Rembrandt® Artists Quality Extra Fine, Holland	Red	Cadmium red light	p(*n*BA/MMA) + CdS, xCdSe + Calcite ($CaCO_3$)	PR 108

Table 1 List of the investigated mock-ups and commercial acrylic paints and their technical properties as declared by the companies. The chemical composition of the binding media and extender were identified in previous studies [~~15~~9, ~~22~~16]

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Sample	Colour	Pigment Classical Name	T_g /°C unaged	T_g /°C aged 31 days	T_g /°C aged 83 days	T_m/°C unaged
Plextol® D498 acrylic emulsion			10.1 °C			54.6 °C
Plextol® D498 + ultramarine blue	Blue	Ultramarine blue	12.2 °C	15.7 °C	19.3 °C	54.9 °C
Plextol® D498 + hydrated chromium oxide green	Green	Hydrated chromium oxide green	10.3 °C	12.5 °C	16.8 °C	
Plextol® D498 + cadmium red	Red	Cadmium red medium	11.8 °C	11.8 °C	13.5 °C	58.3 °C
Liquitex® / Professional Acrylic artist color, USA/Canada	Blue	Ultramarine blue	7.0 °C	10.2 °C	10.7 °C	39.0 °C / 43.3 °C
Liquitex® / Professional Acrylic artist color, Usa/Canada	Green	Chromium oxide green	10.3 °C	11.6 °C	19.3 °C	38.6 °C / 43.8 °C
Liquitex® / Professional Acrylic artist color, USA/Canada	Red	Cadmium red light	6.4 °C	10.4 °C	10.8 °C	38.5 °C / 44.9 °C
Rembrandt® / Artists Quality Extra Fine, Holland	Blue	Ultramarine blue	9.4 °C	11.0 °C	19.4 °C	
Rembrandt® / Artists Quality Extra Fine, Holland	Green	Chromium oxide green	10.8 °C	19.7 °C	19.6 °C	
Rembrandt® / Artists Quality Extra Fine, Holland	Red	Cadmium red light	9.8 °C	18.5 °C	18.7 °C	

Table 2 Differential scanning calorimetry/ic (DSC) results of the mock-ups and commercial acrylic paints before ageing and after UV ageing for 31 and 83 days: glass transition T_g /°C temperatures and melting temperature T_m /°C of the non-ionic surfactant

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Sample	T_{onset}/°C degradation unaged	Unaged Mass/% of the organic component	Unaged Mass/% of the residue component	T_{onset}/°C degradation aged 31 days	Aged 31 Mass/°C of the organic component	Aged 31 Mass/% of the residue component	T_{onset}/°C degradation aged 83 days	Aged 83 Mass/% of the organic component	Aged 83 Mass/% of the residue component
Plextol® D498 acrylic emulsion	299	92	8						
Plextol® D498 + ultramarine blue	311	64	36	264	64	36	121	45	55
Plextol® D498 + chromium oxide green	323	83	17	322	83	17	323	83	17
Plextol® D498 + cadmium red	297	80	20	335	80	20	337	81	19
Liquitex® / Blue Professional Acrylic artist color/ USA/Canada	82 / 189 300	47	53	251	44	56	250	42	58
Liquitex® / Green Professional Acrylic artist color/ Usa/Canada	84 / 185 295	43	57	290	39	61	277	38	62
Liquitex® / Red Professional Acrylic artist color/ USA/Canada	80 / 186 303	54	46	304	53	47	309	53	47
Rembrandt® / Blue Artists Quality Extra Fine/ Holland	86 / 178 298	55	45	274	52	48	239	48	52
Rembrandt® / Green Artists Quality Extra Fine/ Holland	86 / 170 275	37	63	310	38	62	311	37	63

Rembrandt® / Red Artists Quality Extra Fine/ Holland	82 / 176 304		64	36	326		63	37	328		63	37

Sample	T_{onset} degradation unaged (°C)	T_{endset} degradation unaged (°C)	Unaged Weight of the organic component (%)	Unaged Weight of the inorganic component (%)	T_{onset} degradation aged 31 days (°C)	T_{endset} degradation aged 31 days (°C)	Aged 31 Weight of the organic component (%)	Aged 31 Weight of the inorganic component (%)	T_{onset} degradation aged 83 days (°C)	T_{endset} degradation aged 83 days (°C)	Aged 83 Weight of the organic component (%)	Aged 83 Weight of the inorganic component (%)
Plextol® D498 acrylic emulsion	299	420	92.33	7.67								
Plextol® D498 + ultramarine blue	311	434	64.04	35.96	264	427	63.54	36.46	121	428	45.07	54.93
Plextol® D498 + chromium oxide green	323	440	83.4	16.60	322	443	82.69	17.31	323	442	82.78	17.22
Plextol® D498 + cadmium red	297	437	79.63	20.37	335	437	79.87	20.13	337	438	80.52	19.48
Liquitex® – Blue Professional Acrylic artist color, USA/Canada	82 - 189 300	443	47.21	52.79	251	444	44.49	55.51	250	440	42.14	57.86
Liquitex® – Green Professional Acrylic artist color, Usa/Canada	84 - 185 295	436	42.53	57.47	290	435	39.47	60.53	277	435	37.92	62.08
Liquitex® – Red Professional Acrylic artist color, USA/Canada	80 - 186 303	431	53.73	46.27	304	432	52.55	47.45	309	430	52.72	47.03

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Rembrandt® – Blue Artists Quality Extra Fine, Holland	86 - 178 298	437	55.19	44.81	274	430	52.01	47.99	239	431	47.83	52.17
Rembrandt® – Green Artists Quality Extra Fine, Holland	86 - 170 275	405	36.99	63.01	310	421	37.73	62.27	311	422	37.37	62.63
Rembrandt® – Red Artists Quality Extra Fine, Holland	82 - 176 304	420	63.66	36.34	326	420	62.71	37.29	328	422	62.67	37.33

Table 3 Thermoal gravimetryic (TG) results of the mock-ups and commercial acrylic paints before ageing and after UV ageing for 31 and 83 days: initial degradation temperature/°C (T_{onset}), final degradation temperature (T_{endset}), and weight mass/% loss percentage (%) of the organic and inorganic residue compounds

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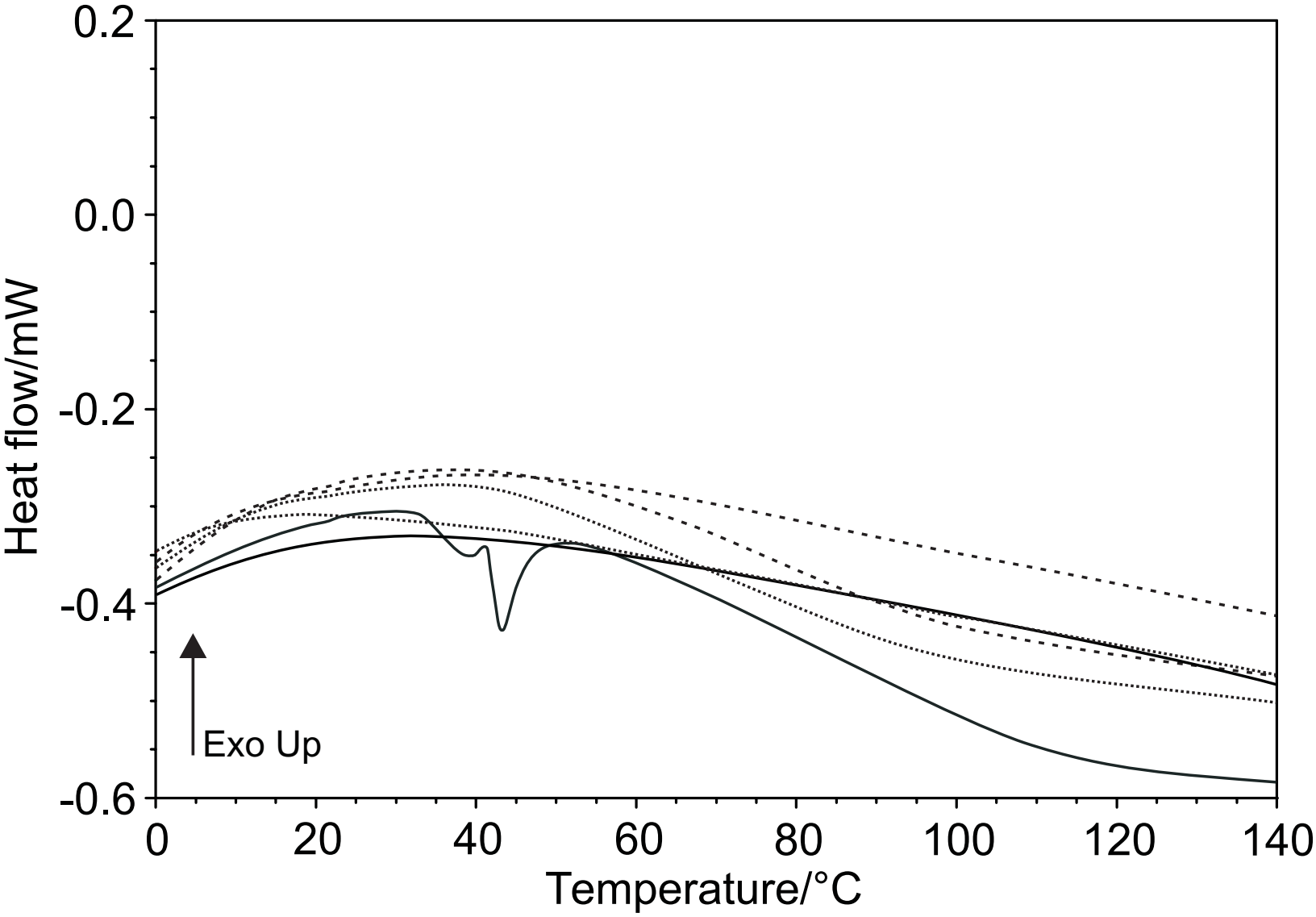
Figure 1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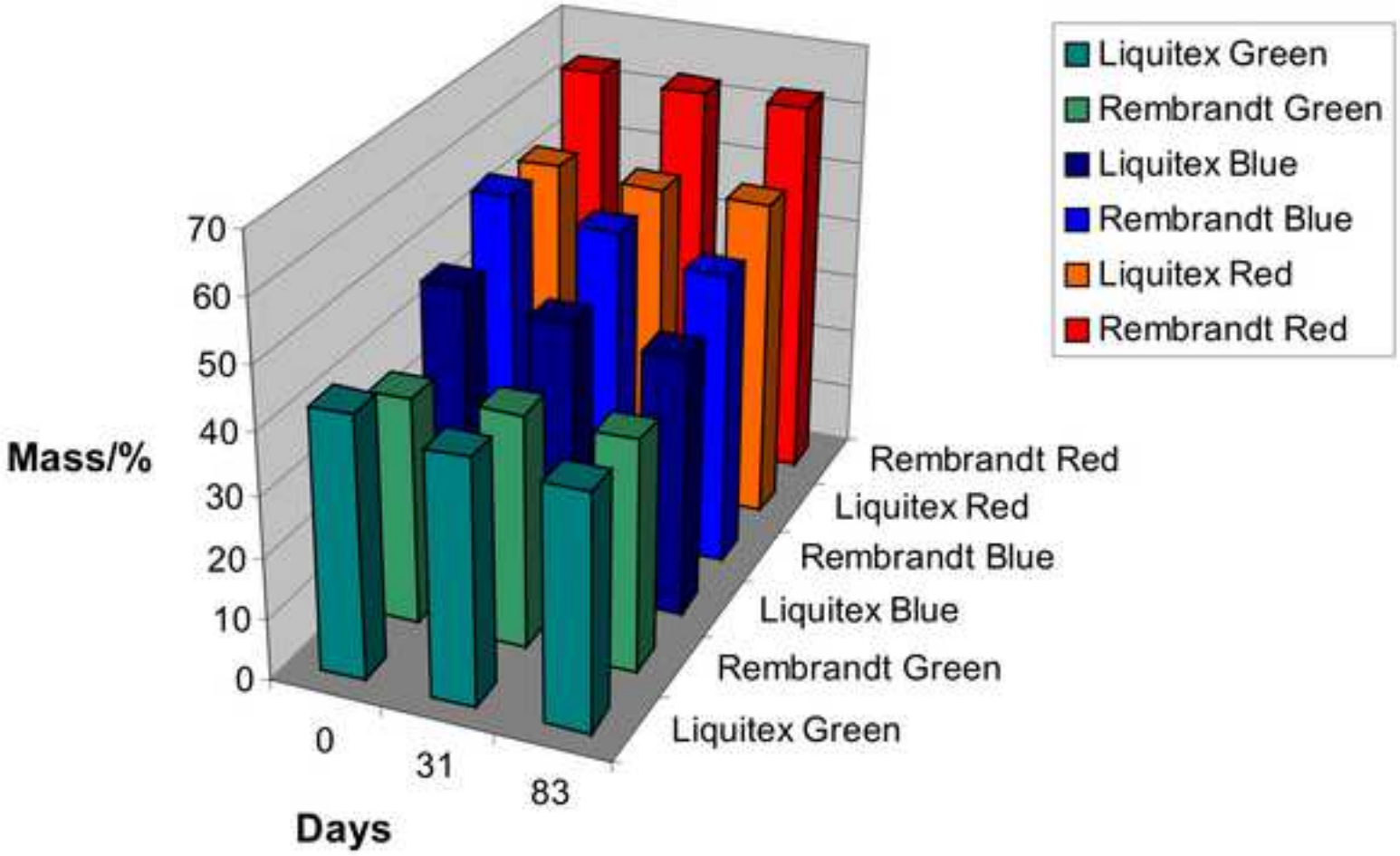

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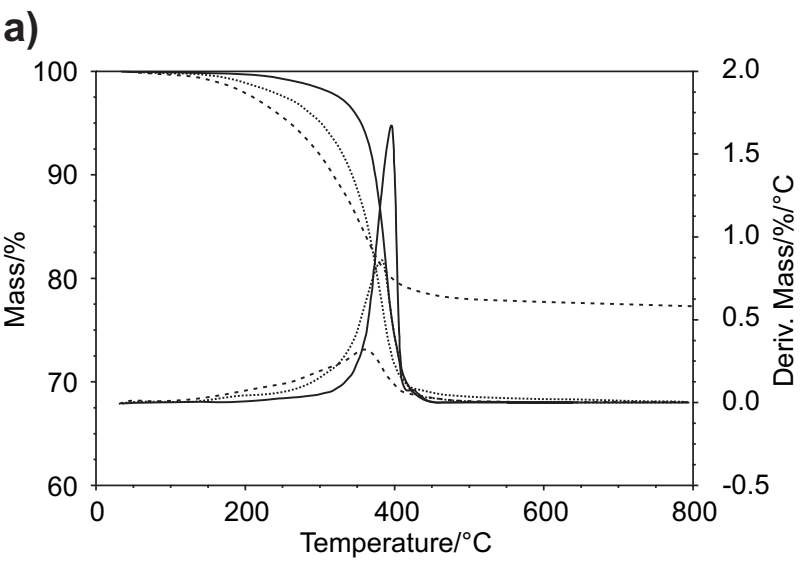
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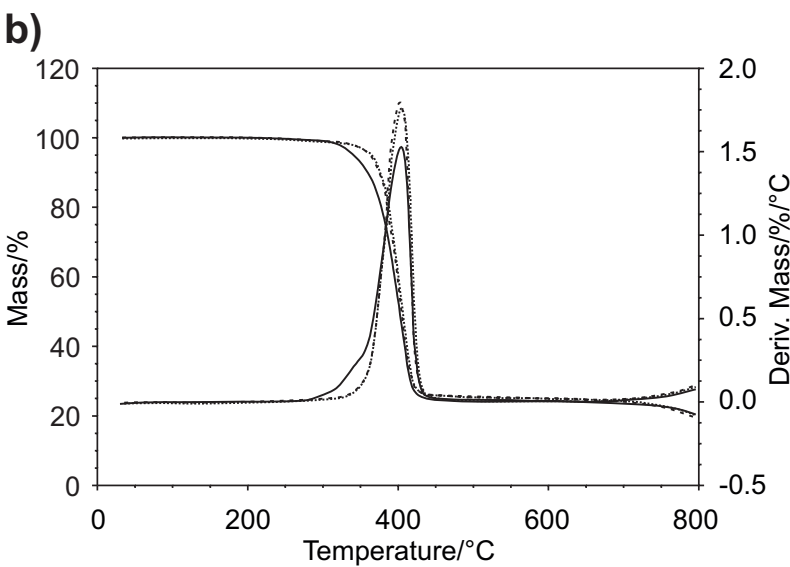
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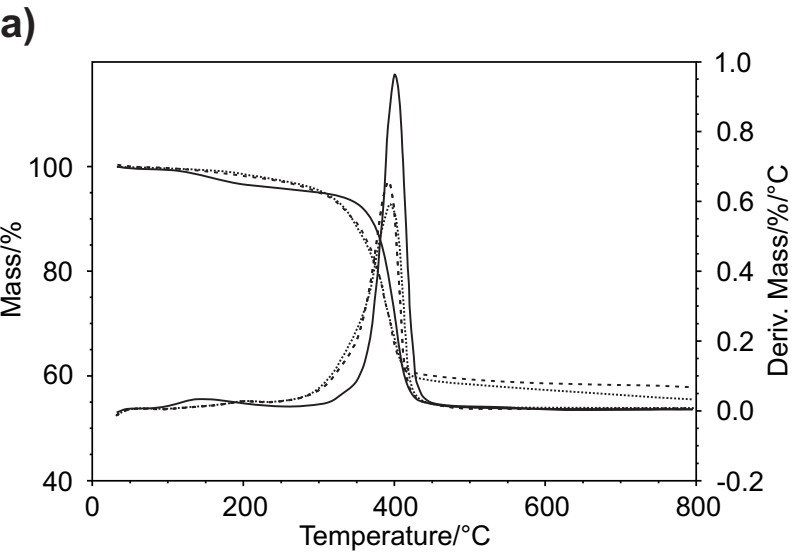
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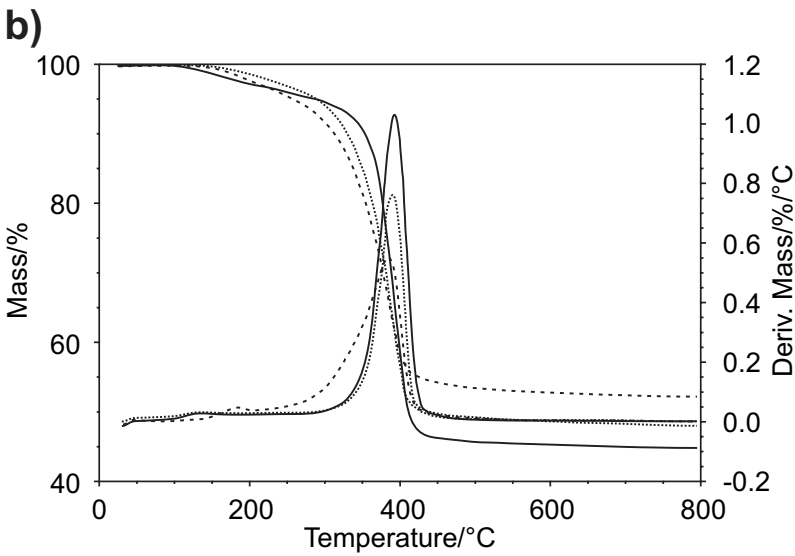
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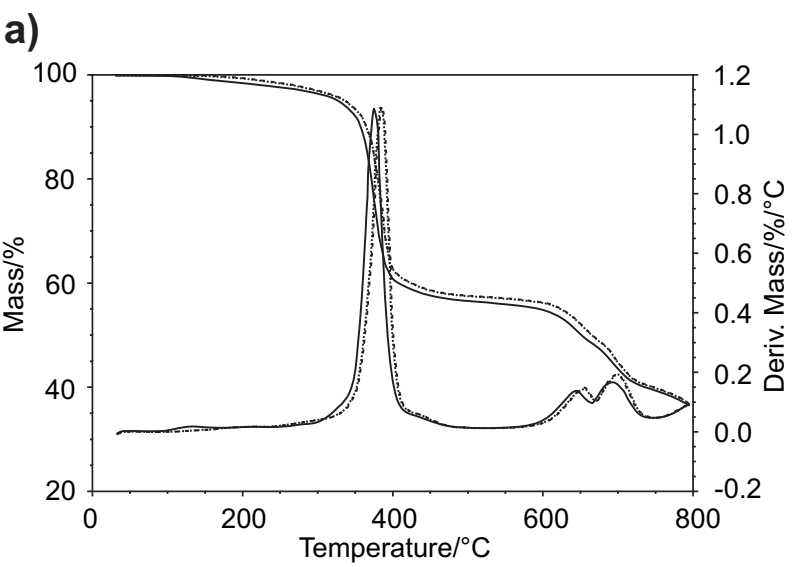
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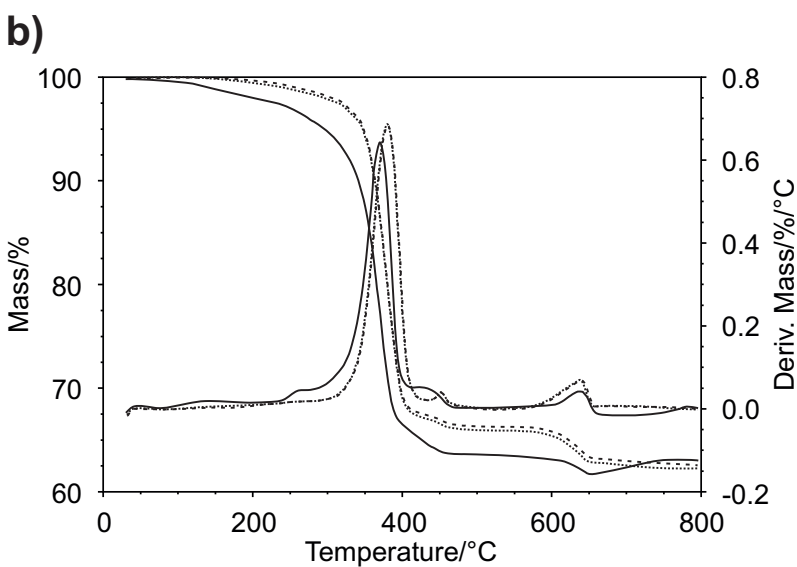
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