Διερευνώντας την επίδραση των λιπαρών συνδετικών στα χάρτινα υποστρώματα των έργων τέχνης

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Investigating the effect of oil mediums on the supports of the works of art on paper

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Περίληψη

Οι λιπαρές ουσίες έχουν ευρέως χρησιμοποιηθεί ως συνδετικά υλικά σε έργα τέχνης σε χαρτί, όπως σε ελαιογραφικά σχέδια και σκίτσα, ελαιογραφίες, ασπρόμαυρα και έγχρωμα χαρακτικά, σε τυπογραφικές εκτυπώσεις, κ.α. Οι συντηρητές χαρτιού έχουν εντοπίσει συγκεκριμένα προβλήματα που σχετίζονται με την παρουσία του λιπαρού συνδετικού σε ελαιοχρώματα ή σε μελάνια εκτύπωσης, όπως απορρόφηση και διάχυση του λιπαρού συνδετικού, η οποία συνοδεύεται με δυσχρωμία και μείωση της μηχανικής αντοχής του υποστρώματος, ευθραυστότητα και ευθρυπτότητα, και κατά συνέπεια απώλεια του ζωγραφικού στρώματος-εικόνας. Σκοπό της έρευνας αποτελεί η εξέταση της επίδρασης των λιπαρών συνδετικών στις οπτικές, μηχανικές και χημικές ιδιότητες των χάρτινων υποστρωμάτων, καθώς και των παραγόντων που προκαλούν ή επιδεινώνουν την εμφάνιση των φαινομένων.

Για το λόγο αυτό, πραγματοποιήθηκαν μελέτες σε αυθεντικά έργα τέχνης και σε δοκίμια που είχαν υποβληθεί σε τεχνητή γήρανση σε κλειστό περιβάλλον, με την εφαρμογή μη-καταστρεπτικών μέθοδων διάγνωσης, οπτικής μικροσκοπίας ανάκλασης και φθορισμού, GC-MS, φασματοσκοπίας ανάκλασης με οπτικές ίνες (FORS), απεικόνισης με μετρητικό μικροσκόπιο DinoLight UV, ηλεκτρονικής μικροσκοπίας σάρωσης (SEM) και δοκιμασίας αντοχής στον εφελκυσμό. Ο συσχετισμός των αποτελεσμάτων δίνει τη δυνατότητα διατύπωσης υποθέσεων για την εμφάνιση των φαινομένων. Τέλος, εφαρμόστηκε πειραματική διαδικασία για την εξαγωγή και ανάλυση πτητικών ενώσεων από τις περιοχές φθοράς, με σκοπό την αξιολόγηση της κατάστασης διατήρησης, καθώς και την επίδραση των υλικών κατασκευής.

Στο συγκεκριμένο πόστερ παρουσιάζοντα μέρος των αποτελεσμάτων που σχετίζονται με την αλλάγή του χρώματος, της διαφάνειας, των χημικών και των μηχανικών ιδιοτήτων που οφείλονται στην παρουσία του λιπαρού συνδετικού στο χάρτινο υπόστρωμα. Οι εργασίες πραγματοποιήθηκαν στα πλαίσια του ερευνητικού προγράμματος με θέμα «Φυσικοχημική μελέτη και τεκμηρίωση της κατάστασης διατήρησης ελαιογραφικών έργων και σχεδίων σε χαρτί. Διαμόρφωση κριτηρίων – Προτάσεις συντήρησης» το οποίο υλοποιήθηκε μέσω του Αρχιμήδης ΙΙΙ - Ενίσχυση ερευνητικών ομάδων στα ΤΕΙ με επιστημονική υπεύθυνο τη Δρ. Αθηνά Αλεξοπούλου.

Fig. 1 Atlas of damage

Abstract

Oil paintings, oil sketches and studies on paper supports, as well as black and white and coloured prints, printed books, etc. present evidence of damage that has been associated with the presence of the oil medium in the paint or the ink used. The most common problems are absorption and diffusion of the oil medium by the paper support, related with discoloration, loss of mechanical strength, fragility and embrittlement of the support, that seem to appear in a random way. However, proved to be a complex matter.

Aim of research is the investigation of the effect of the oil medium to the optical, mechanical and chemical properties of the paper support, as well as of the parameters that trigger and/or aggravate the occurence of the phenomena of damage. Research was performed to original artworks and artificially aged mock ups, involving non destructive imaging documentation and digital Dino Light UV microscope, optical microscopy and UV microscopy, colorimetry, spectroscopy and FORS (optical Fibres), SEM-EDX and Head Space Solid Phase Micro Extraction combined with GC-MS, as well as tear resistance testing, to map and record the areas of damage and to provide hypothesis for the occurence of the phenomena caused by the absorption of the oil binder by the paper support upon ageing. Only part of the results are presented in this poster, those related with the changes of colour, transparency, mechanical properties, as well as the emission of VOC from artificially aged mock ups and original artworks.

Research was carried out through a project entitled "Oil paintings on paper support: Documentation of the state of preservation using multispectral imaging and chemical analysis. Determination of evaluation criteria - conservation treatment proposals", which was aimed at the investigation and physicochemical documentation of the problems occurring in oil paintings on paper supports" within the framework of the operational program "Archimedes III: Funding of Research Groups in TEI of Athens", organised and conducted by the Laboratory of Physical Chemical Methods for Diagnosis – Documentation of the Department of Conservation of Antiquities and Works of Art in the Technological Educational Institution of Athens, with scientific responsible Dr. Athena Alexopoulou.

Fig. 2 **Head space vials in the ageing oven**

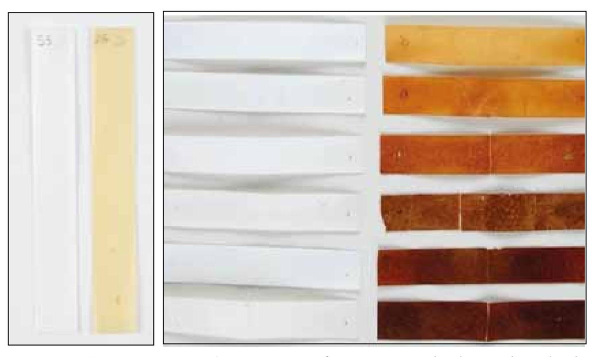


Fig. 3 **Cotton mock ups.** Left: Non oiled and oiled mock ups before ageing. Right: From the tope to the bottom, the mock ups at 1, 4, 7, 14, 21 and 28 days of ageing.

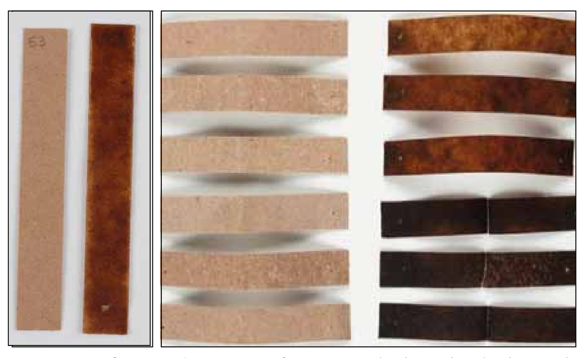


Fig. 4 **Kraft mock ups.** Left: Non oiled and oiled mock ups before ageing. Right: From the tope to the bottom, the mock ups at 1, 4, 7, 14, 21 and 28 days of ageing.

Fig. 5 **Montval mock ups.** Left: Non oiled and oiled mock ups before ageing. Right: From the tope to the bottom, the mock ups at 1, 4, 7, 14, 21 and 28 days of ageing.

Types of damage

The most common problems associated with the presence of the oil binder in paint or printing media on the works of art on paper support are the following:

a) absorption of the oil medium by the paper support, sinking on the verso side of the work, locally and overall.

b) diffusion of the oil medium beyond the limits of particular areas of colour or printed lines or letters of ink, either b/w or colour.

c) discoloration of the support related to the absorption of the oil medium

d) Loss of mechanical strength, fragility and embrittlement.

Oil absorption and discoloration could be general, varying in intensity locally, rarely uniform, usually responding to areas which are more worked, executed in thicker paint layers, or certain colours. A common phenomenon is the appearance of discoloration beyond the limits of the areas of paint, beyond specific colour areas, due to the diffusion of the medium. However, discoloration is usually recorded solely on the verso of works and it varies from case to case. The discoloured paper support, gradually loses its mechanical strength, becomes weak and brittle and breaks locally or in parts.

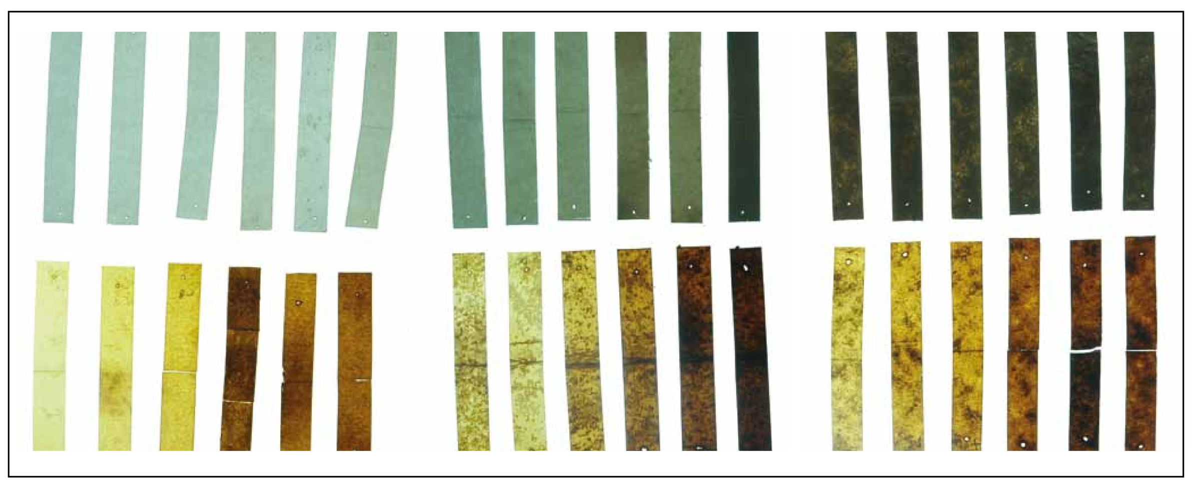


Fig. 6 **Trasmitted light photography.** Top row: sets of cotton, motval and kraft plain paper mock ups in 1, 4, 7, 14, 21and 28 days of ageing. Lower row: sets of oiled cotton, motval and kraft paper mock ups at all ageing periods.

Experimental

Three types of paper were investigated: a) cotton pHoton™ high purity paper by the Munktel paper Mill, 80gsm (Conservation by Design Limited, UK), b) Canson® Montval® watercolour paper, 185gsm (Art & Hobby, Greece and c) Kraft paper (Dionisopoulos - local paper distributer in Greece), 135 gsm. These papers were chosen because they had fibre content and characteristics similar to some of the works of art from the National Gallery in Athens being investigated in this project. Half the mock ups were impregnated with cold pressed linseed oil (Windsor & Newton, London) after weighing. Strips were suspended on cotton threads in headspace vials above 5ml of 15% sodium chloride for analysis solution and aged at 90oC at 78% RH for 1, 4, 7, 14, 21 and 28 Days.

The effect of oil application on the transparency of the paper was studied with the measurement of the lux levels of light transmitted by the plain and oiled mock ups at every stage of ageing with a digital lightmeter.

The change of colour was measured using the CIE L*a*b* (CIELAB) colour space, following the TAPPI standard T524om-94. The L*a*b* measurements were performed with a Lovibond Reflectance tintometer.

The degradation of cellulose caused by the presence of linseed oil on paper was investigated with the use of GC-MS analysis of the volatile organic compounds (VOC) emitted from paper samples, with and without oil application, in the various stages of a close environment artificial ageing program.A preconditioned SPME needle was inserted into a headspace vial containing the paper sample immersed in 5ml of 15% sodium chloride solution and incubated for 40 minutes. The SPME needle was then retracted and reopened in the injection port of the GC-MS and heated to 230oC for 10 minutes to release the volatile components and trap them at the beginning of the column.

The changes in the mechanical properties of the oiled paper supports were examined with tear resistance measurments using an Elmendorf-type apparatus (ISO 1974, 1990).

Transparency

The plain paper mock ups of the three paper types present completely different behaviour, regarding the changes of the intensity of light passing through the mock ups upon ageing. This can be due to the different fibre and pulp content and distribution, but also to the changes in morphology upon ageing. On the other hand, the oiled mock ups of the three types of paper present similar behaviour upon ageing and their measurement values are getting quite close in the 14, 21 and 28 days of ageing. This could indicate that linseed oil inputs a common behaviour in the three types of paper as far as the intensity of light passing through the mock ups upon ageing is concerned. The results indicate that the oil application increases the transparency oof the three paper types.

The refractive index value of a solid film of linseed oil rises slightly with age, causing slightly more scattering perhaps which subsequently means that the paper would allow less light to pass through. However, the morphological changes upon ageing cause much greater changes to the system, increasing the light scattering , so the mock ups appear to be less transparent with age as the oil film shrinks within the system.

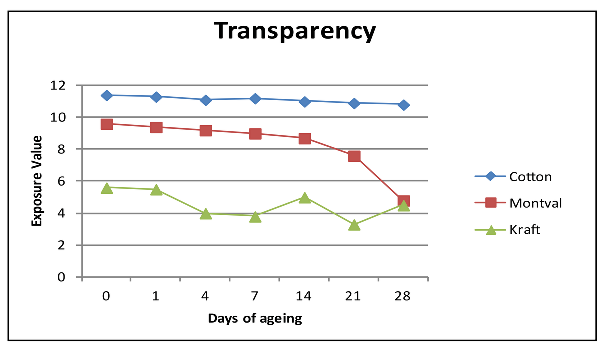


Fig. 7 Measurments of the light intensity passing through the plain cotton, montval and kraft paper at all ageing periods.

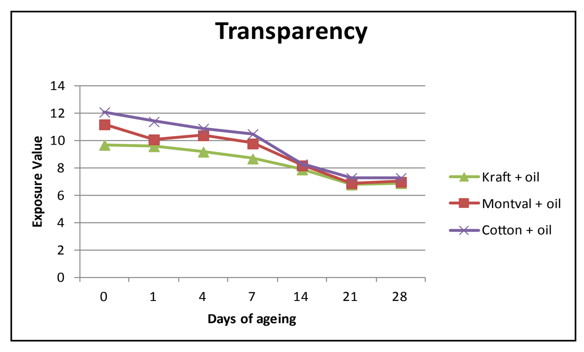
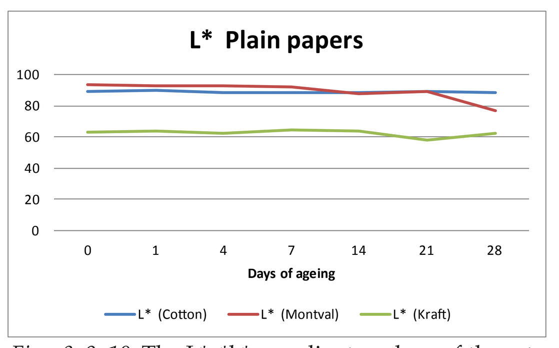


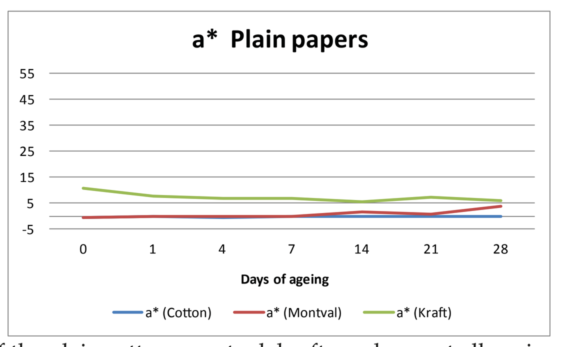
Fig. 8 Measurments of the light intensity passing through the oiled cotton, montval and kraft paper at all ageing periods.

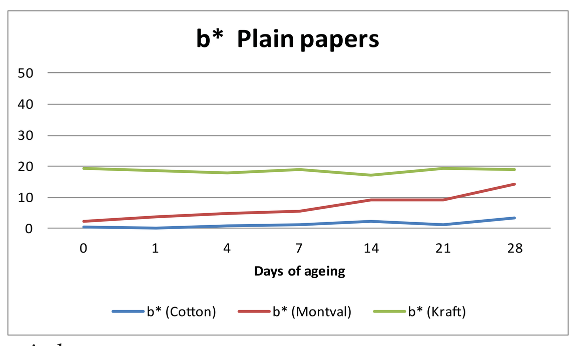
Colour changes

It is likely that linseed oil application is principally responsible for the colour changes during ageing, though oxidation of the cellulose in the paper may also contribute to the colour change, especially if the oil is enhancing the rate of oxidation of the paper, as indicated in the VOC emission studies. This is more evident in the white mock ups of cotton and watercolour paper that present a similar pattern of variations of the L*a*b* coordinates values upon ageing. However, results indicate that fibre and paper pulp content, the colour and the weight of the paper influence these values. In addition, the behaviour of oil film upon ageing, which gradually shrinks and recedes from the surface of the paper revealing the fibre net, subsequently affects the optical properties and colour appearance of the mock ups.

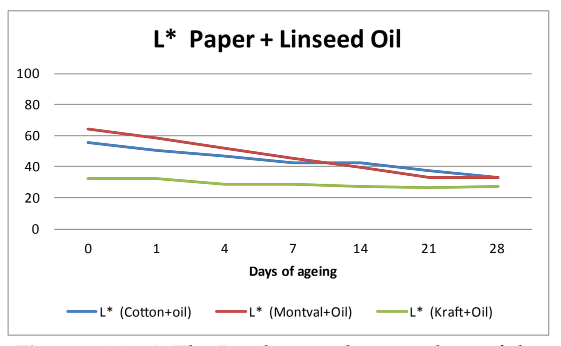
In all three paper types, oil application results in the significant reduction of brightness, and analogous decrease of yellow colour upon ageing. For the white colour papers the increase of the red colour, and the fluctuation pattern within that, could be indicative of the chemical changes. Also differences in colour through each mock up are strongly associated with the oil concentration on the paper locally.

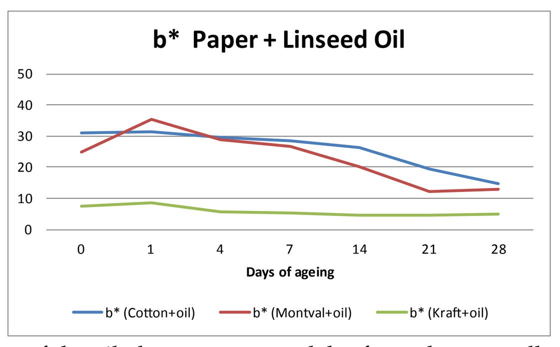


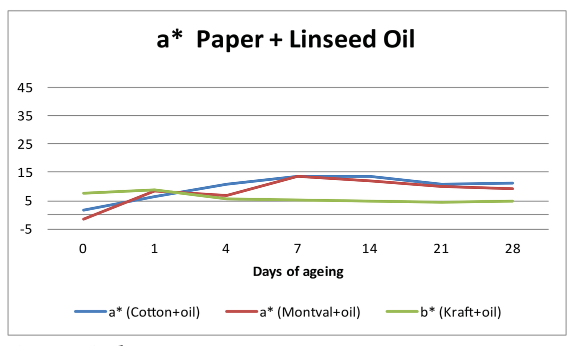




Figs. 8, 9, 10. The L*a*b* coordinate values of the sets of the plain cotton, montval, kraft mock ups at all ageing periods.







Figs. 11, 12, 13. The L*a*b* coordinate values of the sets of the oiled cotton, montval, kraft mock ups at all ageing periods.

Mechanical properties

Tear resistance measurments in plain and oiled cotton paper mock ups before ageing procedure indicated that paper mock ups become stronger after the application and drying of the oil for 40 days. This is in accoradance with the observation of the visual examination that the oiled mock ups appear stiffer and more resilient. It could be suggested that as the fibres bonded within the dried elastic polymer, a kind of elasticity and extra strength is provided to the support.

Tear resistant measurements in plain and oiled cotton paper mock ups after 28 days of ageing, indicated that mechanical strength of the oiled mock ups reduces dramatically, while for the plain paper that is limited. Loss of mechanical strenght was apparent during visual examination, since even carefull handling of the mock ups could cause damage to the mock up. Shrinkage and loss of elasticity of the oil film upon ageing in combination with the degradation of cellulose caused by the presence of the oil could justify the phenomena recorded for the oiled mock ups. It has been recorded that cracking or breaking of the support in the original works of art on paper occurs in the areas where oil absorption appears to be more intense. Thus, further investigation is required to investigate the parameter of the oil quantity absorbed by the paper in the changes of the mechanical changes properties of the support. In addition, VOC analysis indicated that oil accelerates more the degradation wood based papers, so the parameter of the fibre content should be investigated as well.

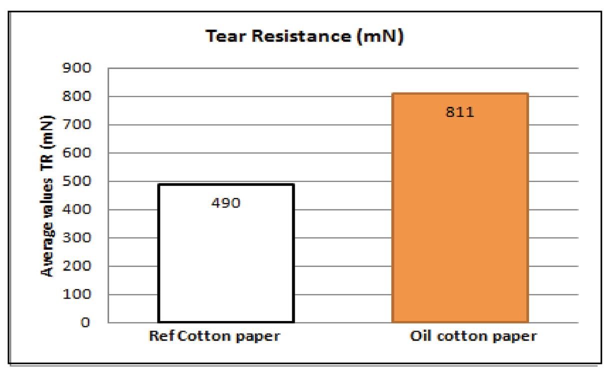


Fig. 14 Average tear resistant values (10) of the plain and oiled cotton mock ups before ageing.

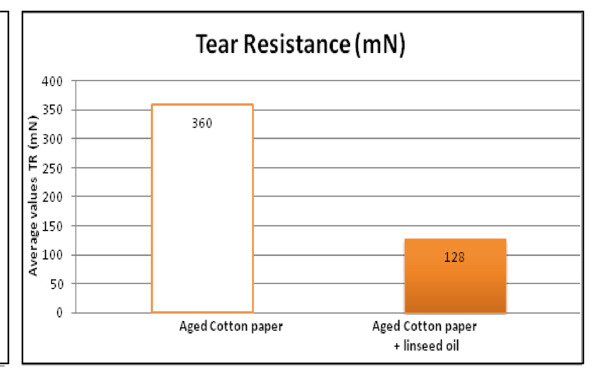


Fig. 15 Average tear resistant values (10) of the plain and oiled cotton mock ups after 28 days of ageing.

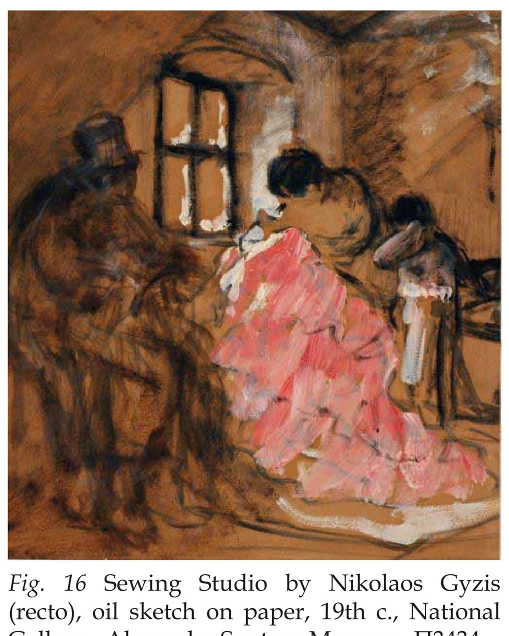


Fig. 16 Sewing Studio by Nikolaos Gyzis (recto), oil sketch on paper, 19th c., National Gallery - Alexander Soutzos Museum, Π3434.

VOC analysis in original artworks

Six original works were selected for this experimental procedure, providing different case studies regarding the technique, the materials and the presence of characteristic phenomena and problems related to absorption and diffusion of the oil binder. The experimental procedure was carried out in the Paper Conservation studio of the National Gallery in Athens. It involved encasing both the artwork and the SPME needle in a glass set up to track the VOCs emitted. The SPME needle was placed on the verso of the work, over a specific area that presented oil absorption, diffusion or discoloration. Then the tip of the needle covered with the glass lid of a petri dish in an attempt to confine the area of extraction, and then the absorbing part of the needle was exposed. The needle was exposed for 24 hours. The SPME needle was then retracted and transferred back to the lab for GC_MS analysis.

Head space analysis of original artworks containing oils gave a similar range of volatile oxidation products products obtained from the mock ups. These products included a large range of aromatic and straight chained aliphatic hydrocarbons, a series of straight chained aldehydes, some volatile carboxylic acids and esters and the range of furan and furfural and furanone derivatives singled out for monitoring for the study of the mock–ups (as these were the compounds given only by paper and not by oil films as they age, i.e. they were exclusive to the oxidation of cellulose). In addition to these compounds some of the works of art gave some compounds derived from coniferous resins and may be because of the presence of rosin size.

VOC analysis of the artifically aged mock ups

The presence of oil in the cotton paper has greatly accelerated the emission of furfural, 2-ethyl furan, 5- methyl, 5- ethyl furfural and 5-pentylfuranone during ageing, while in the wood based papers has greatly accelerated the emission of furfural, 5-methy furfural, 5-ethyl furfural and 5-pentylfuranone.

It could be concluded that for the cotton paper at least dried linseed oil in the paper greatly accelerates and increases the emission of volatile cellulose degradation products and therefore it is reasonable to assume, that since cotton paper is almost pure cellulose and that the chemistry of drying oils are similar to that of linseed oil,probably other drying oils increase the rate at which cellulose in paper degrades.

Similarly, for the wood based paper, dried linseed oil greatly accelerates and increases the emission of cellulose degradation products and therefore it is reasonable to assume, that drying oils increase the rate at which cellulose in wood based paper degrades.

Furfural emissions are greater from wood based paper impregnated with linseed oil compared to furfural emissions from cotton paper impregnated with linseed oil. The increased levels of furfural are an indication that the lignin and/or hemicelluloses present in the wood based papers are accelerating the degradation even further in the presence of oil. It can be speculated that furfural is a favoured product of cellulose degradation in the presence of oil.

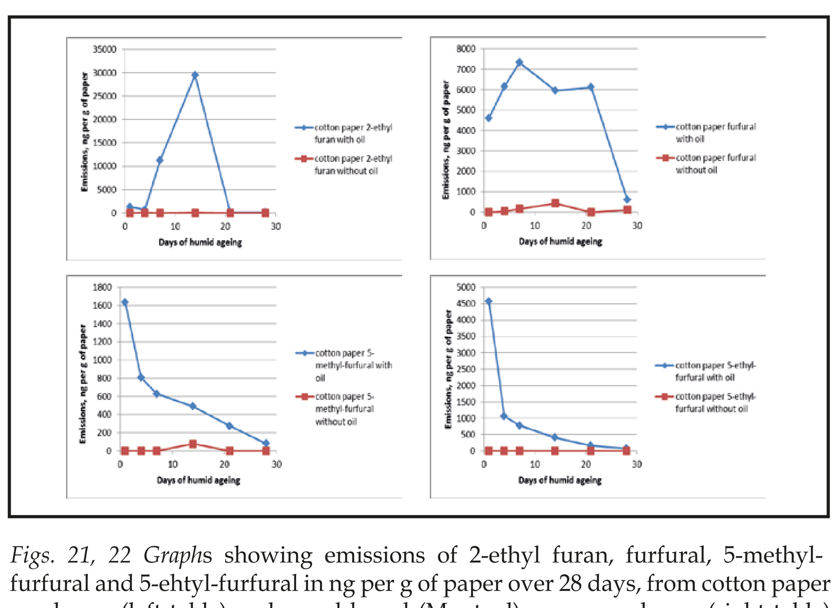
However it seems that in the wood based paper the amount of furfural produced is increased whereas the levels of the other four compounds studied seems to decrease. Perhaps at least part of the decreased levels can be explained by the lower percentage of cellulose present in wood based papers and that the increased levels of furfural are an indication that the lignin and/or hemicelluloses present in the wood based papers are accelerating the degradation even further in the presence of oil.

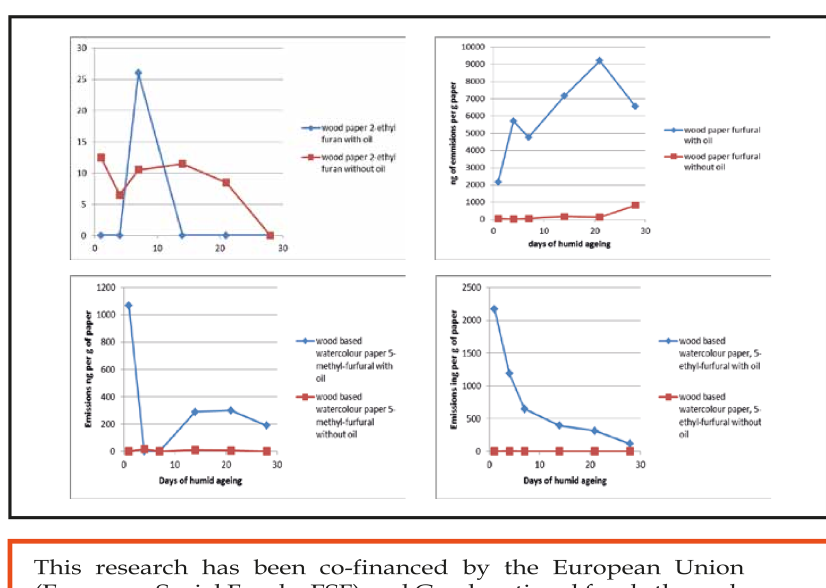
Fig. 17 Sewing Studio, Π3434 (verso), the position of the SPME needle is noted with the white arrow, while the glass lid with a red circle

Figs. 18, 19. The red circle on the top detail marks the position of the glass lid on the *verso*

	Target Compounds	Typical Retention time	Object 3434	Object 2985	Object 9812	Object 9822	Object 9823	Object 9740
			Peak area Responses					
1	ethanoic acid	2.20	0	0	0	0	0	18749
2	toluene	5.03	2666	225377	270175	225377	224072	1259
3	hexanal	6.45	1410	1800	4558	1800	3268	2570
4	furfural	8.74	712	1419	1062	1419	968	0
5	m-xylene	10.66	2960	52171	107032	52171	3791	7794
6	n-nonane	12.95	166417	50821	160541	50821	248265	3561
7	pentanoic acid	-	59720	2248	3486	2248	1325	7474
8	verbenene	15.65	83730	59977	39690	59977	47808	36174
9	1,2,4-trimethyl-benzene	17.51	7011060	2381114	5624232	2381114	2965459	4050050
10	phenol	17.79	165482	39974	28192	39974	9013	0
11	n-decane	17.97	8951804	1211161	806214	1211161	1180410	3320455
12	n-octanal	18.13	1428623	2112976	4389190	2112976	2062575	1333866
13	limonene	19.02	4097780	1167206	1006624	1167206	918811	5628112
14	nonanal	21.95	10709155	7859229	14706906	7859229	7230586	6833445
15	heptanoic acid	22.83	175085	150100	79565	150100	23741	121170
16	trans-verbenol	23.36	214054	53468	35064	53468	60694	559247
17	menthol	24.16	771216	376790	305389	376790	238675	692205
18	napthalene	24.27	64962	35948	60341	35948	43137	18167002
19	octanoic acid	24.53	107918	337591	42063	337591	0	202842
20	decanal	25.20	7624114	5024242	13101169	5024242	4461035	3743096
21	I-verbenone	25.35	63019	42403	14515	42403	22311	379792
22	5-butyldihydro -2(3H) furanone	26.81	76039	100798	246471	100798	66220	256265
23	nonanoic acid	27.33	0	0	0	0	0	0
24	5-pentyl-2(5H)-furanone	29.16	11590	1459	0	1459	1773	21129
25	vanillin	30.65	127211	41540	31411	41540	2436	374493
26	2,2,4-trimethyl-1,3-pentanediol diisobutyrate	35.41	12429860	9849237	8918838	9849237	7366720	12915752
27	isopropyl myristate	40.32	432675	255378	228216	255378	142827	325486

Fig. 20 List of the VOC emitted from six original art works from the National Gallery's - Alexandros Soutzos Museum collections.





Figs. 21, 22 Graphs showing emissions of 2-ethyl furan, furfural, 5-methyl-furfural and 5-ethyl-furfural in ng per g of paper over 28 days, from cotton paper mock ups (left table) and wood based (Montval) paper mock ups (right table) with and without linseed oil application.

This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: ARCHIMEDES III.
Investing in knowledge society through the European Social Fund.

from the National Gallery in Athens being investigated in this project. Half the ups were impregnated with cold pressed linseed oil (Windsor & Newton, London weighing. Strips were suspended on cotton threads in headspace vials above 15% sodium chloride for analysis solution and aged at 90oC at 78% RH for 1, 4, 7 and 28 days.

The effect of oil application on the transparency of the paper was studied with the m ment of the lux levels of light transmitted by the plain and oiled mock ups at every s ageing with a digital lightmeter.

The change of colour was measured using the CIE L*a*b* (CIELAB) colour space, fol the TAPPI standard T524om-94. The L*a*b* measurements were performed with bond Reflectance tintometer.

The degradation of cellulose caused by the presence of linseed oil on paper was i gated with the use of GC-MS analysis of the volatile organic compounds (VOC ted from paper samples, with and without oil application, in the various stag close environment artificial ageing program.A preconditioned SPME needle w from the National Gallery in Athens being investigated in this project. Half the ups were impregnated with cold pressed linseed oil (Windsor & Newton, London weighing. Strips were suspended on cotton threads in headspace vials above 15% sodium chloride for analysis solution and aged at 90oC at 78% RH for 1, 4, 7 and 28 days.

The effect of oil application on the transparency of the paper was studied with the m ment of the lux levels of light transmitted by the plain and oiled mock ups at every s ageing with a digital lightmeter.

The change of colour was measured using the CIE L*a*b* (CIELAB) colour space, fol the TAPPI standard T524om-94. The L*a*b* measurements were performed with bond Reflectance tintometer.

The degradation of cellulose caused by the presence of linseed oil on paper was i gated with the use of GC-MS analysis of the volatile organic compounds (VOC ted from paper samples, with and without oil application, in the various stag close environment artificial ageing program.A preconditioned SPME needle w