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EVALUATION OF THE EFFECTS OF CYCLODODECANE ON OIL PAINTINGS

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Abstract

The solubility of oil paint components during the application of cyclododecane in solvent mixtures was evaluated in order to predict if the application of cyclododecane during restoration may significantly alter the chemical state of the paint layer in oil paintings. The chemical affinity between some of the oil binder components and non-polar cyclododecane could potentially lead to interactions or leaching during the application. In order to investigate these effects a set of samples taken from oil paintings from the early 1900s and 2008, were treated with cyclododecane in a solution, melted, and sprayed as aerosol. The samples were also submitted to a comparative extractive treatment with cyclododecane and organic solvents of different polarities. After the treatments, the extracted components were analysed by gas chromatography-mass spectrometry (GC/MS), which provided detailed molecular information on the composition of the extracts, together with a quantitative profile of fatty acids in extracted triglycerides, after saponification and derivatisation. The results show that applications of cyclododecane both as a spray and in a saturated solution in a hydrocarbon solvent determine the extraction of a low amount of lipids from the paint. On the other hand, when cyclododecane is applied in the melted form, there is an extraction of lipid components of the paint into the treatment solution.

Keywords*: Oil paintings; Cyclododecane; Gas-chromatography-mass spectrometry; Fatty acids; Organic solvents.*

Introduction

Cyclododecane (CDD) is a saturated cyclic alkane with the structural formula $C_{12}H_{24}$. It was first used for conservation in 1995 in Germany [1]. It is used as a temporary adhesive, consolidant, fixative and hydrophobic layer [2].

Cyclododecane can be used as a temporary consolidant and coating, thanks to its ability to sublimate in environmental conditions, making the treatment reversible.

CDD is soluble in non-polar organic solvents and almost totally insoluble in water and other polar solvents [3]. This confers water repellency to the surfaces where it is applied.

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For these reasons, CDD has been experimented with for many applications including wall paintings, stone materials, archaeological finds, paper, textiles and paintings on canvas and wood [4-9].

In terms of its use on canvas paintings, few studies have investigated the physical behavior of the paint layers during and after the treatment. The parameters evaluated include the penetration level, water repellency, and the sublimation time, which has been estimated in the range of a few days for sprayed film or weeks when melted cyclododecane is applied. This range depends on the thickness and environmental conditions [10-12]. In addition, other studies reported evaluations of the CDD behavior as sealing and hydrophobizing coating on canvas [13].

However, little is known regarding the interactions of CDD with binders in the paint layers and few publications underline how further tests are necessary to explore this aspect [14].

The possibility of unknown interactions between the cyclododecane and the paint layer during the treatment, and the risk of solubilization or leaching of some components of the paint layer through the action of cyclododecane solutions or melted cyclododecane, probably explain the limited number of cyclododecane case studies on easel paintings [15-19], compared to other fields.

More detailed studies on the interactions of the CDD with paintings on canvas include those by Gudrun Hiby [3, 10, 12], who specifies how preliminary trials are needed to verify interactions of CDD with oil and varnish layers, especially if these layers are recent. This is done in order to decide whether the application of this hydrocarbon is opportune and to adopt the most suitable application mode.

In order to further explore these aspects, and to make some recommendations concerning the use of CDD in this field, we tested whether the application of cyclododecane in solution, spray or melted, could lead to physical-chemical variations in an oil paint layer.

Some interactions, such as a potential leaching effect, may occur due the chemical affinity between the non-polar cyclododecane and the lipid components of the oil paint layer, which initially form a water-repellent film of low polarity.

In recently-applied oil films, there is a low percentage of compounds derived from oxidative scission, occurring during the polymerization/curing of the medium. On the other hand, there are still many not polymerized triglycerides, which are characterized by low polarity. Non-polar solvents and cyclododecane can potentially solubilize, or partially solubilize these components, thus causing swelling, or mobilization of lipid components in the paint films.

Leaching is responsible for increased fragility and loss of physical properties of the paint film, if non-bonded compounds are extracted from one layer to another. Non-bonded low molecular weight components (LMWs) confer flexibility to the paint film, by acting as plasticizers. It is well known that low molecular weight material is extracted during cleaning [20-21] and even during other conservation treatments, such as a varnish application on oil paintings [22-24].

We investigated the effect of cyclododecane during restoration procedures, where it was employed as consolidant, adhesive or temporary hydrophobic coating, by conducting extraction experiments on naturally-aged paint. The rationale underlying our experiments was to assess whether CDD or CDD solutions can act an effect of partial solubilization, and to determine the least invasive type of CDD application (melt, spray or solution).

A total of 18 specimens were examined, taken from oil paintings on canvas with: one century of ageing (early 1900s) and a few years of ageing (2008). The paint samples were treated with cyclododecane applied in different modes and compared with paint samples treated with only solvents. The samples were chemically characterized in order to obtain information on the molecular profile of the organic materials in the paint layer and of those extracted in the solutions used for the cyclododecane treatment.

In fact, as shown in literature, the quantities of soluble material, and rate of extraction, depend on factors including the age of the paint film, as well as the solvent used [23-25].

The profile of the fatty acids in the paint layers were investigated using an analytical technique suited to the quantitative characterization of organic materials at a molecular level: gas chromatography-mass spectrometry (GC/MS). The profile of fatty acids and their amounts were determined after the saponification of triglycerides and derivatisation with a silylatyng agent [26].

The characterization of the glycerolipids included an evaluation of the characteristic chemical parameters commonly used to investigate oil paint films. Firstly, the ratio between the percentage content of palmitic acid and stearic acid (P/S), which is different for the three traditionally most common drying oils - linseed, walnut and poppyseed [27]. Secondly, the ratio between the content of azelaic and palmitic acids (A/P), indicative of the advancement of the oxidation-reticulation processes involving 9-insaturated fatty acids. Thirdly, the ratio between the content of the unsaturated C18 oleic acid and the saturated C18 stearic acid (O/S), which gives an estimation of residual unsaturated acyl chains, in despite of oxidation process which involve reactions in correspondence of the double bonds. Finally, the sum of the amounts of dicarboxylic acids sebacic, azelaic and suberic (ΣD %), which is considered as another index of the degree of curing and oxidation [26] and infact the quantities of soluble material, and rate of extraction, depend on factors including the age of the paint film, as well as the solvent used.

In order to assess the possible tendency of CDD and of CDD solutions to extract lipid components from the paint, the samples of oil paintings on canvas were treated with cyclododecane as spray and melted. Subsequently the paint samples were also submitted to an extractive treatment with organic solvents of different polarities: ligroin, xylenes (mixture of ortho, meta and para isomers) and mixtures of CDD in ligroin. This latter to test also the interaction of the CDD applied in solution form. The component mobilized into the solutions was analyzed by GC/MS.

The experimental design was inspired by application conditions that are found in literature [21-24].

The solubility parameters of these two solvents selected in this experimentation reflect the influence of polar and non-polar interactions in the physical process of solubilization. The three parameters Fd, Fp and Fh denote dispersion forces, polarity and hydrogen bonding respectively, and are conventionally shown graphically in a Teas diagram used to compare solvents in the conservation field [28].

According to the values reported in the literature, ligroin and xylenes have different interactions with linseed oil. Ligroin, with Fd 97, is an almost completely non-polar solvent. Its solvent power is hence limited to non-polar substances. On the other hand, xylenes, characterized by a Fd value of 83 [29], lower than that of ligroin, are slightly more polar. This implies a higher extraction capacity towards relatively more polar lipid components, such as di-carboxylic acids, which are formed as a result of oxidative cleavage and phenomena due to ageing.

As a result of the ageing and polymerization, the solubility zone of the linseed oil passes from an Fd value of 45-90 for fresh linseed oil, to an Fd value of 50-75, corresponding to medium polarity, for the aged oil [30-32].

For these reasons, these solvents were chosen as a comparison term in which to insert the CDD, which does not know the real Fd value.

Experimental

Samples

These samples comprise uniform oil films and their canvas, obtained from two oil paintings.

The 18 samples analyzed were collected from one oil painting dating from the early 1900s, and from one prepared in 2008 and then naturally aged.

Nine samples, group Op (old painting, with one century of ageing), were taken from an oil painting of the early 1900s, by an unknown artist, which was kindly provided by the conservator, Enrica Boschetti, for research purposes [33]. No information was available on the technique employed. However, visual investigations indicated the use of an industrial white pre-primed canvas and a commercial oil paint.

Another nine samples, group Yp (young painting, with three years of ageing), were from an oil mock painting, prepared at the University of Studies Urbino (Italy), in 2008 by one of the authors [33]. The paint was prepared by depositing monochromes and homogeneous layers of tube-paint (Maimeri Classico, Italy) on a sized linen canvas with two preparation layers, one containing only gypsum and animal glue (this latter prepared 1:9 in water, mixed by volume), the other with the addition of pre-polymerized linseed oil (unknown trademark). Between the preparation and the paint layer a thin layer of priming with a solution of animal glue in water (1:8, mixed by volume) was applied.

The samples were taken from each painting from a limited area with similar pigmentation and texture. The size of the samples, which included canvas and preparation, was 0.7 x 3.7cm with a weight of between 0.12 and 0.18 grams.

Before the extraction treatment, to test the application of CDD in a melted form and as a spray, two samples for group were covered with CDD in aerosol spray and with solid pure CDD after melting, respectively. The excess of cyclododecane, depositing on the surface, was removed with a scalpel prior to immersion in vials with solvent, for not alter the concentration of the solution.

Extractive treatments

Cyclododecane (CTS srl, Italy), cyclododecane spray (Hans Michael Hangleiter, Gmbh), ligroin (Carlo Erba, Italy), not denaturated, with a certified aromatic content below 0.01%, with a boiling point 80-120°C, and xylenes (VWR, Italy) with a boiling point 135-140°C, were used for the extractive treatments.

In order to assess the possible tendency of CDD to extract lipid components from the paint, the samples of oil paintings on canvas were treated with an extraction treatment with solvent mixtures and cyclododecane in different application modes: solution in non-polar solvent, spray, and melted.

For the paint layers treated with CDD in spray and melted, ligroin 100%, was selected as a solvent for the extraction, for its high non-polarity and the low interaction with the paint layers. In this case the immersion in solvent was necessary to evaluate an extractive effect by CDD applied in solid form (spray and melted). However the variations found in the extract are attributable to treatment with CDD in spray and melted.

The others paint layers were submitted at the extractive treatment with organic solvents of different polarities: ligroin, xylenes and mixtures of CDD in ligroin, this latter to test the application of CDD in solution. Some of the samples were treated only with the immersion in ligroin and xylenes solvents as a comparison of the potential extractive effect of the CDD (Fig. 1).

The choice of these solvents was motivated by their solubility parameters. In fact, xylenes are aromatic solvents with a lower polarity than ligroin.

Xylenes were selected because a certain extraction of fatty acids was expected from these solvents, contrary to the ligroin a non-polar solvent. For this reason, have been select both to compare the extractive capacity of cyclododecane, of which do not know the current Fd. Therefore, there were prepared several mixtures of the two solvents and cyclododecane to carry out an extractive treatment on the samples.

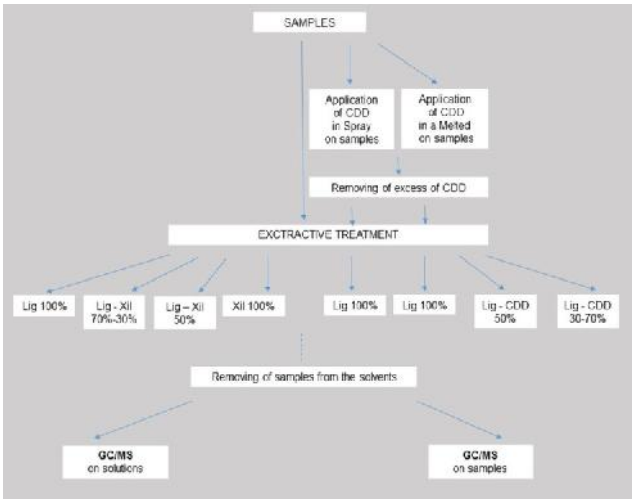

Fig. 1. Scheme of the experimental design for the extraction treatment. Preparation of samples; CDD application in spray form and in a melted; Extractive treatment; GC/MS, gas chromatography/mass spectrometry system.

The following six solutions were prepared:

ligroin 100% (v)
ligroin-xylenes 70-30% (v/v)
ligroin-xylenes 50% (v/v)
xylenes 100% (v)
cyclododecane-ligroin 50% (w/w)
cyclododecane-ligroin 70-30% (w/w)

The extraction tests involved the immersion of the samples in a vial with 7mL of each solution which was then placed in a hot water bath at 60°C for 30 minutes (Fig. 2).

Fig. 2. Vials with different solutions in which the samples are immersed

The duration of the water bath was carried out in order to facilitate the extraction and maintain the CDD in solution, in fact, especially in concentrations of 50% and 70% in ligroin, this one tends to recrystallize immediately into the solvent [7, 9].

These extreme conditions, concerning the ratio of solvent amount than the sample, were indispensable to induce quantifiable and measurable amounts of material extractable from the oil binder into the solvents [21, 23], correlated to the phenomena occurring during the practical use of CDD in conservation, when it is applied in a hot solution to increase it solubility in solvents and facilitate its penetration into the surfaces [5, 8, 34].

At the end of the extraction treatment, the samples were removed and placed in a glass desiccator, with a controlled atmosphere, which was obtained with a saturated solution of sodium chloride (NaCl), at RH 50-75%, for six months. Throughout this period, the samples were weighed to check the sublimation of cyclododecane, until a constant weight. After this period, both the treated paint samples and the solvent solutions were analysed by GC/MS.

The code "Yp" (young painting, with three years of ageing) and "Op" (old painting, with one century of ageing), was used for the solutions followed by the abbreviation of the respective treatment. Table 1 summarizes the painting samples and their treatments were submitted to.

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Table 1. Samples and treatment applied to the oil paintings.
Yp: young painting, three years of ageing; Op: old painting, one century of ageing.

Painting sample code	Treatment	Solution code
Untreated	None	-
Yp1	Ligroin 100%	Yp Lig
Yp2	Xylenes 100%	Yp Xil
Yp3	Xylenes-Ligroin 50%	Yp Lig-Xil 50%
Yp4	Ligroin-Xylenes 70-30%	Yp Lig-Xil 70-30%
Yp5	CDD applied as a melt prior to immersion in Ligroin 100%	Yp Lig CDDm
Yp6	CDD sprayed prior to immersion in Ligroin 100%	Yp Lig CDDs
Yp7	Ligroin-CDD 50%	Yp Lig-CDD 50%
Yp8	Ligroin-CDD 30-70%	Yp Lig-CDD 30-70%
Untreated	None	-
Op1	Ligroin 100%	Op Lig
Op2	Xylenes 100%	Op Xil
Op3	Xylenes-Ligroin 50%	Op Lig-Xil 50%
Op4	Ligroin-Xylenes 70-30%	Op Lig-Xil 70-30%
Op5	CDD applied as a melt prior to immersion in Ligroin 100%	Op Lig CDDm
Op6	CDD sprayed prior to immersion in Ligroin 100%,	Op Lig CDDs
Op7	Ligroin-CDD 50%	Op Lig-CDD 50%
Op8	Ligroin-CDD 30-70%	Op Lig-CDD 30-70%

Reagents

All solvents were Baker HPLC grade. Fatty acids, hydrochloric acid (HCl), potassium hydroxide (KOH), hexamethyldisilazane (HMDS) and N,O-bis(trimethyl)silyltrifluoro-acetamide (BSTFA) containing 1% trimethylchlorosilane (TMC), which is a catalyst of esterification and etherification reactions with BSTFA, and therefore is automatically included by the manufacturers in the formulation of BSTFA [35], as well as the internal standard for derivatisation, tridecanoic acid (C13) and the internal standard for injection, hexadecane (ED), were supplied by Sigma Aldrich (USA).

A solution of fatty acids in acetone, used as a standard, was prepared by weighing the pure acids. The solution contained: lauric acid (3.49µg/g), suberic acid (3.6µg/g of Su), azelaic acid (3.47µg/g of A), myristic acid (3.32µg/g of My), sebacic acid (3.25µg/g of Se), palmitic acid (3.7µg/g of P), oleic acid (4.94µg/g of O), and stearic acid (5.57µg/g of S). All acids,

purity > 99%, were purchased from Sigma-Aldrich (USA). Cyclododecane (industrial purity) was donated by CTS (Italy).

Gas chromatography

The analytical procedure used for this study was based on a method for the analysis of the glycerolipidic fractions from complex cultural heritage materials [26, 36-39].

For paint samples, 1- 1.4mg of paint from the uppermost layer were scraped off with a scalpel, placed inside a closed Teflon vial, and subjected to saponification with 300µL of ethanolic KOH (KOH in EtOH/H_2O 10% w/w). The reaction took place in a microwave oven model MLS-1200 MEGA Milestone at a temperature of 80°C for 60min, using a power of 250W.

After saponification, neutral organic components were extracted with n-hexane (3× 500µL) and, after acidification with hydrochloric acid (concentration 10M; acidification to pH~2), the organic components were extracted from the hydrolysate with diethyl ether (3× 500µL).

For the analysis of leached materials in the solvent solution and in CDD solutions, 2mL of liquid was taken from the solutions, put in a Teflon vial, dried under a continuous flow of nitrogen, to constant weight and then subjected to saponification and extraction in the same conditions.

Aliquots of the extracted acidic fraction were evaporated to dryness under nitrogen flow and subjected to derivatization prior to the quantitative analysis. The derivatization was performed with 20µL of N,O-bis(trimethyl)silyltrifluoro-acetamide (BSTFA) and 150µL iso-octane as a solvent, at 60°C for 30min. Prior to injection into the column, tridecanoic acid and n-hexadecane were added as internal standards. A quantity of 2µL of the resulting solution was injected into the GC/MS and analyzed. For each sample, the analyses were conducted in duplicate.

The analyses were performed on a 6890N GC System Gas Chromatograph (Agilent Technologies), coupled with a 5973 mass-selective detector single quadrupole mass spectrometer equipped with a PTV injector. Chromatographic separation was performed on an HP-5MS fused silica capillary column coupled with deactivated silica pre-column. The carrier gas He, was used in the constant flow mode at 1.2mL/min. The PTV injector was used in splitless mode at 300°C. The chromatographic oven was programmed as follows: 80°C, isothermal for 2 min, 10°C/min up to 200°C, 200°C, isothermal for 3min, 10°C/min up to 280°C, 280°C isothermal for 3min, 20°C/min up to 300°C and 300°C, and isothermal for 30min.

The mass spectrometer was operated in the electron impact (EI) positive mode. The mass spectrometer transfer line temperature was 280°C; ion source temperature was at 230°C, while the quadrupole temperature was at 150°C.

For quantitative determinations, a standard solution of pure fatty acids was used. Calibration curves for each fatty acid were obtained before GC/MS analyses. The data acquisition was obtained in SIM mode (selected ion monitoring).

Results and discussion

For a quantitative assessment of leachable lipid material, both paint samples and solvent aliquots of the solutions used for the extractions were analyzed by GC/MS.

The GC/MS analysis of fatty acids in the solutions used for the extractive treatments revealed that the amount of lipids leached from old and young paint systems showed a similar trend compared to the type of solvent used, as seen in Figure 3. The reproducibility of the analytical procedure permits to evaluate as strongly significant the variations of 20% or more [37].

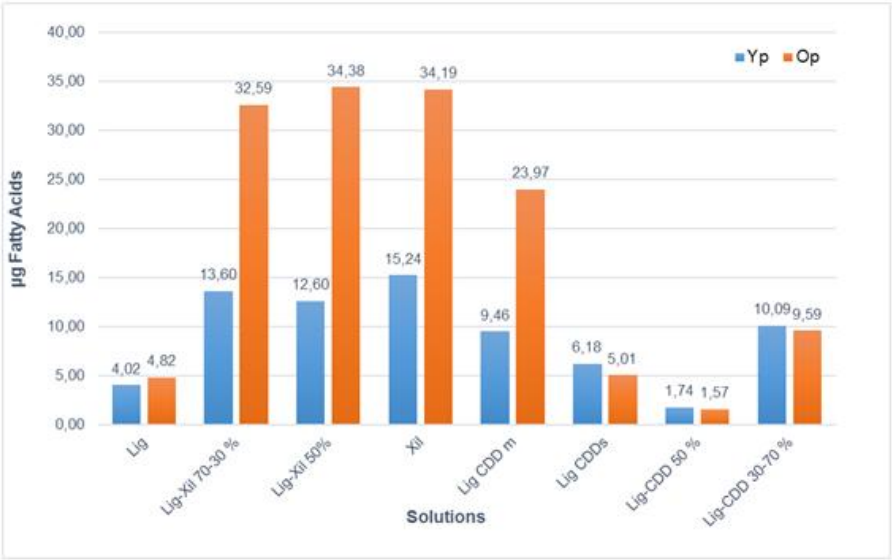

Fig. 3. Total amount of leached fatty acids during treatment with xylenes, ligroin solvents and CDD. Yp: young painting, three years of ageing; Op: old painting, one century of ageing

The most dramatic effects are caused by the xylene solutions and by xylenes plus ligroin solutions, which seem to extract the highest amount of fatty acids. However, the extractive action seems to be carried out mainly by the xylenes, in fact the total amount of fatty acids in the ligroin was very low.

In contrast, all CDD-treated samples showed lower amounts of leached fatty acids. However, when compared to the samples immersed in ligroin alone, the application of CDD, to some extent facilitates the extraction of the LMW material. The effect is more pronounced for the application of the melted product (lig-CDDm). This suggests that in the case of the molten CDD application, the effect could be heat-induced, and the temperature promotes the movement and extraction of free fatty acids.

In addition, a comparison between the Yp and Op solutions with xylenes, ligroin-xylenes, and ligroin after application of melted CDD (lig-CDDm) show that the values were double and almost triple for the Op solutions. For these solutions, which feature a consistent extraction power, the total amounts of fatty acids extracts extracted from the old painting (Op) is higher than those of the young painting (Yp): it appears that ageing, in the painting of the early 1900s, has produced more easily extractable fractions of free fatty acids and non-bonded dicarboxylic acids.

However, the GC/MS results of the paint samples, summarized in Table 2, show that the ratios between palmitic and stearic acids are in the same range for both group Yp and group Op samples respectively.

A higher amount of lipids seems to be extracted from the 1900 painting, which suggests that the aged paint contains more free fatty acids and dicarboxylic acids available for extraction, as a result of degradation due to ageing.

Differences appear when analyzing the content of dicarboxylic acids and the values of A/P and O/S ratios. The A/P ratio of the extracted lipid material appears to significantly increase in the samples treated with cyclododecane, and more significantly in the samples of the group Yp, where it arrives up to 4.7% for the extraction performed after the treatment with spray cyclododecane. The increase in the content of dicarboxylic acids in the extract can be explained with the fact that a preferential extraction of non-polar free saturated acids as palmitic

acid during the CDD treatment. This explanation is supported in the Yp group paint samples, by the smaller variability registered for the O/S ratios, which provides information on the number of double bonds still available for oxidation. In fact, if paints with higher A/P values were more oxidized, the O/S values would have shown a decrease due to the transformation of oleic acid into azelaic acid. On the other side, in the obtained results show that there is no decrease of the O/S ratio, which remains stable near to 0.8 or in some cases slightly increases, up to 1.2. This suggests that CDD treatment does not lead to an oxidation but influences the solubilization behavior of fatty acids. A higher mobilization and extraction rate can be observed for fatty acids with longer alkyl chains such as palmitic acid and stearic acid, due to the interactions between the saturated alkyl chains in triglycerides and CDD.

Table 2. Characteristic parameters of untreated and treated paint samples.
P/S: palmitic acid vs stearic acid, A/P: azelaic acid vs palmitic acid,
O/S: oleic acid vs stearic acid, ΣD: sum of dicarboxylic fatty acids azelaic, sebacic and suberic.

Samples	Treatment	P/S	A/P	O/S	ΣD(%)
Untreated	None	1.2	1.2	0.8	35.8
Yp1	Ligroin 100%	1.5	1.7	1.1	44.6
Yp2	Xylenes 100%	1.5	2.1	1.3	48.4
Yp3	Xylenes-Ligroin 50%	1.2	1.3	1.7	32.1
Yp4	Ligroin-Xylenes 70-30%	1.4	1.6	1.9	37.8
Yp5	CDD melt	1.4	1.8	1.1	66.5
Yp6	CDD spray	1.0	4.7	0.8	66.5
Yp7	CDD in ligroin 50%	1.2	3.9	0.9	64.1
Yp8	CDD in ligroin 30%	1.4	2.8	1.2	56.2
Untreated	None	0.9	1.9	0.4	46.8
Op1	Ligroin 100%	1.1	1.6	0.6	43.9
Op2	Xylenes 100%	1.0	2.6	0.4	56.8
Op3	Xylenes-Ligroin 50%	0.9	2.5	0.4	52.8
Op4	Ligroin-Xylenes 70-30%	0.9	4.0	0.3	65.2
Op5	CDD melt	1.1	2.2	0.1	56.3
Op6	CDD spray	0.8	1.7	0.0	47.0
Op7	CDD in ligroin 50%	1.1	3.5	0.1	66.8
Op8	CDD in ligroin 30%	1.0	3.9	0.1	69.1

However, in terms of the total amount of dicarboxylic acids ΣD (%), found in paint samples after extractive treatment, one trend was highlighted. The higher relative content of dicarboxylic acids was found in samples that had undergone CDD treatment, compared to untreated paint. This can be explained by the fact that the addition of CDD displaced the residual non-bonded triglycerides containing nonpolar acyl chains acid from the paint layer.

Conclusions

The analytical investigations conducted in the current study have highlighted how treatment with cyclododecane is not entirely devoid of interactions with the oil binder of the paint layer on which it is applied. However, this phenomenon is influenced by the degree of ageing of the painting, and by the application mode of cyclododecane.

Regarding the solubilization effect by cyclododecane, concentrations and application methods are the most important parameters to be controlled. Nevertheless, CDD has a less invasive effect on the oil binder than bi-component solutions of polar/non-polar solvents, in this case ligroin and xylenes in different percentages, or a xylenes solution with a higher polarity.

Comparing the several methods of applying CDD to a painting, a 50% solution of cyclododecane in ligroin and the spray application of CDD seem to be best choices. These applications lead to a very low amount of extracted fatty acids. In the case of the spray CDD, the fatty acids extracted were even lower than with 100% ligroin solution. In fact, ligroin is a strongly non-polar solvent, and is thus widely used in oil paintings. The molten CDD seems to

offer the lower safety level, likely due to the local heating effect when the CDD is applied, which facilitates mobilization, leaching and extraction.

It is not easy to generalize empirical recommendations based on experimental studies carried out on models, nevertheless an indication, based on this preliminary investigation of the effect of CDD application on oil paintings, would be to use CDD solutions in highly non-polar solvents with a maximum concentration of 50%, or alternatively to apply CDD as a spray onto the painting.

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