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Evaluation of Green Solvents' Applicability for Chromatic Reintegration of Polychrome Artworks

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Abstract: Organic solvents are commonly used in restoration treatments, including chromatic reintegration on polychrome artworks. They are often toxic, and their vapors have a high impact on the environment and restorers, possibly causing pathological conditions. Therefore, this study aims at defining a new green solvent that can be used for chromatic reintegration, maintaining the volatility and the desired physical–chemical properties. The dispersion forces value (F_d) of ethyl lactate was taken as reference for a comparison with the proposed solvents, since it was found to be the most used solvent for the dilution of Maimeri Restoration Colors (MRC) and Gamblin Conservation Colors (GCC). Based on the Teas fractional parameters, six solutions based on acetals and ethanol have been proposed and tested. They were mixed with both MRC and GCC, and applied on prepared canvases. The difference between the backgrounds made with reference solvent and the one made with the proposed alternatives was evaluated through spectrocolorimetric measurements. Fourier-transform infrared spectroscopy in the attenuated total reflectance mode (FTIR-ATR) was performed on the applied layers to evaluate the presence of residual solvent inside them, while the volatility of the solvents was assessed by performing gravimetric analysis. The study showed that acetals, acetals' blends, and acetals–ethanol mixtures represent suitable alternatives for the dilution of Gamblin Conservation Color and Maimeri Restoration Colors.

Keywords: chromatic reintegration; acetals; sustainability; Gamblin; Maimeri; green; solvent

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1. Introduction

Paintings may suffer injuries during their history, which may lead to damage to their paint layers, resulting in a change or reduction in the value that we attribute to the work. It can be of different entities and, typically, the losses of pictorial layers are defined with the Latin term "lacunae" (from the lat. lacuna «lagoon; cavity; lack») [1]. The debate on chromatic reintegration issues is still heated today. By acting on the aesthetic value of the work, it also influences how the painting is perceived by the observers. Hence, the decision of "whether" and "how" to reintegrate is always well-thought-out [2]. Over time, different restoration theories have been proposed, influencing the idea of intervention at both a methodological and conceptual level. Among the many treatments carried out during the restoration of polychrome artworks, the problem of chromatic reintegration certainly represented the foundation of a debate that has not yet ended.

Before the XVIII century, the principles governing the reintegration treatment were very different from those that are generally accepted today by restorers. Previously, greater importance was given to the functionality of the work of art, and it was consequently chosen whether to limit the replenishing of the missing parts or modify the work by incorporating new ideas into the original. Very often, even where the conservative intervention was not necessary or had little reason to exist, works of art were transformed according to the conceptions and needs of the time. It was during the XX century, with the "International Conference for the study of Scientific Methods in the Examination and Preservation of Artworks", held in Rome in 1930, that the first international guidelines for the practice were proposed [2]. These guidelines summarize the thoughts of the personalities who have marked the history of the theory of modern restoration:

- Study of the state of the art of the object before the intervention;
- Limiting the chromatic reintegration to the lacunae;
- The need for the restoration material to be removable;
- Precise description and documentation of the treatment.

In the second half of the XX century, the debate on the reintegration of polychrome artworks became fervent. The main issue was twofold: the need to reconstruct the paint layer where the damage is too extensive or includes parts of the painting that are considered significant for the conveying of the meaning, without creating a false or deceiving the observers. In Italy, restoration theoreticians such as Cesare Brandi and Umberto Baldini proposed new methodologies of intervention, based on the use of neutral tints or hatching comprising different colors [3,4]. The selection of the suitable technique had to be made according to the entity and the position of the lacunae within the artwork. Where the loss is very large and it is not possible to formulate a reconstruction hypothesis, neutral tints or the "astrazione cromatica" technique had to be used, while hatching was considered the most suitable method to restore the figuration.

The overarching principle was to reinstate the visual uniformity of the artwork by performing a reintegration that had to be recognizable from the original—at least at a close look—while not preventing the correct fruition of the work.

It is not possible to define a generalized strategy for the reintegration of polychrome works of art [5]. Even though the hatching techniques are still used today, the methodology has undergone significant developments over the years. Today, the reintegration of the lacunae is also carried out by reproducing the missing part exactly [6].

Although each object has its history and different characteristics, all these methods involve the chromatic reintegration of the artwork's losses only. The range of possible binders to be used is quite broad, varying from acrylic to watercolors, according to the specific needs of the artwork and its original execution technique. However, the colors mostly used in the reintegration of panel and canvas paintings and wooden sculptures are varnish-based [6,7]. Indeed, these polychrome artworks—from the Middle Ages until today—present a varnish layer on the surface with the threefold purpose of protecting and brightening the artwork and saturating the colors [8]. Thus, the application of varnish colors allows for the reaching of approximately the same refractive index as the original areas [9,10]. Terpenic resins such as dammar and mastic have been traditionally used as varnishes by dissolving them in turpentine essence [8]. Even though they are still used today, the introduction of new synthetic low-molecular-weight resins such as urea-aldehydic and hydrocarbon resins (Laropal® A81 and Regalrez®) generated a breakthrough in the world of conservation [11–13]. Both terpenic and these new synthetic varnishes are solutions based on solvents that evaporate during drying, thus creating the dry film on the painting's surface [8]. Generally, petroleum derivatives (shellsol, ligroine, mineral spirits), essential oils derived from turpentine, alcohols, dowanol PM, ethyl lactate, or mixtures of them are used for colors' dilution, based on the desired volatility and aesthetic appearance of the dry color [14–17]. Many of these organic solvents have issues related to their inherent high toxicity, posing risks both for the environment and the health of the operator [18,19].

They have different physical parameters and properties according to their molecular formula and their structural features [20]:

- Evaporation rate;
- Density (kg/m^3);
- Diffusion (m^2/s);
- Vapor tension (kPa);

- Boiling point (°C);
- Melting point (°C).

Such parameters must be taken into consideration to evaluate both the toxicity of organic solvents and the suitability for their use in conservation practices, based on the features required for the specific kind of treatment.

The danger of a solvent can also be evaluated based on the threshold limit value (TLV), which reflects health regulations applied for the protection of industrial workers possibly exposed to the action of solvents [21]. This parameter is defined as the concentration of the substance that can be inhaled for five days (eight hours per day) by most people without adverse effects. The concentration is expressed in parts per million (ppm), i.e., parts of valor (gas) per million parts of contaminated air by volume at 25 °C and atmospheric pressure. A low value (i.e., below 25) shows high toxicity. A value between 50 and 100 corresponds to an average toxic level, while low-toxic solvents are found between 100 and 1000 [18]. Long exposure to some organic solvents' vapors can lead to the onset of different types of pathology in the long term, such as the following:

- irritative effects on skin and mucous membranes;
- effects on both female and male reproductive spheres;
- carcinogenic/mutagenic effects.

They enter the body through contact with skin or inhalation due to their lipophilic nature [22]. The degree of toxicity and danger for the operator depends on numerous factors, including the combined use of different solvents and the chemical–physical properties of the solvent. In most cases, the restorer cannot work under a fume hood, even though air suction and exchange systems are fundamental tools for guaranteeing the operator's safety. The restorer should also wear personal protective equipment (PPE), such as gloves and solvent filter masks, which are, however, rarely used in common practice [23].

The regulations on the production and use of solvents are continuously updated and new rules are drawn up to control the entry of chemical substances into the market (i.e., REACH, CPL, Regulation No. 1272/2008/EC), forcing manufacturers to change the chemical composition of their products, including paints, varnishes, and solvents already on the market. Therefore, it has become necessary to find more sustainable alternatives to be used in the restoration sector as well [24–27].

This study aims at identifying a green solvent able to replace more toxic organic solvents that are currently used in the dilution of varnish colors while maintaining their chromatic and gloss values, as well as their physical parameters as far as possible. The research focused on the evaluation of acetals, acetals blends, and acetals–ethanol mixtures as possible alternative solvents. Acetals are described by an $R_2C(OR')_2$ structure that is formed by the reversible nucleophilic addition of an alcohol to a ketone or an aldehyde. They can be considered promising sustainable alternatives to many toxic organic solvents that are still used in the conservation sector. Indeed, they are bioderived and inherently safer for the operator and the environment, as described in previous work by Macchia et al. (2022) [28,29].

2. Materials and Methods

As a first step, an interview was conducted involving 14 restorers of different ages who had graduated from Italian higher education schools to understand which materials and techniques are used in restoration laboratories and what the needs of restorers are regarding the choice of solvents for the reintegration phase. In the interview, the restorers were asked to explain their approach in the chromatic reintegration of polychrome works of art, mainly consisting of panel and canvas paintings. Specifically, they were asked to provide information on the type of colors and solvents used, as well as the operating procedure.

The interviews highlighted the restorers' common practice, which directed the research towards the characteristics required of the sought green solvent. Based on the survey, two different varnish colors were used in this study:

- Gamblin Conservation Colors (Ultramarine Blue PB29);
- Maimeri Restoration Colors (Cobalt Aluminium Oxides PB28).

The Gamblin Conservation Colors (GCC) are based on the urea-aldehydic varnish Laropal® A81 and are sold diluted in a little bit of mineral spirits. This low-molecular-weight resin is produced by BASF, via reaction of formaldehyde, isobutyraldehyde, and urea in acidic conditions, followed by an alkoxy treatment [30].

The Maimeri Restoration Colors (MRC) are based on mastic, a terpenic resin, and are sold diluted in a little bit of turpentine essence. Mastic is a natural resin produced as a vegetable's exudate by the *Pistacia lentiscus*, a plant that grows typically on Chios Island [31].

As for the solvent used for the dilution of both GCC and MRC, most of the interviewed restorers appeared to prefer ethyl lactate, which seems to be used also by European conservators for this scope, similarly to dowanol PM, mixtures of ethyl lactate, ligroine and isopropanol, or ethanol [17]. For this reason, ethyl lactate was used as a reference solvent to compare its solubility parameters with the ones of the proposed solvents.

2.1. Selection of Alternative Green Solvents

The Teas Solubility Triangle was used to evaluate which of the acetals/acetals' blends/acetals–ethanol taken into consideration show a similar F_d value to the reference solvents [32]. Ethyl lactate was selected as a reference for the solubility parameters.

Since both the solubility and the volatility of the proposed solvents play a significant part in the selection process, the solubility parameters and the boiling points were used to define the most suitable relative percentages of the tested mixtures through a simple system of equations, even though the vapor pressure (kPa) also has to be taken into consideration. Indeed, this parameter is particularly significant to define the evaporation rate of a solvent. Table 1 shows the lowest vapor pressure of ethyl lactate, meaning that it does not evaporate quickly, while other solvents or blends that are commonly used in the conservation practice for chromatic reintegration have higher values to a greater or lesser extent.

Table 1. References (REF) and selected alternative solvents and solvents' mixtures. Blends' boiling points were calculated as the weighted mean of the values corresponding to the constituents.

ID	Mixture	Relative Proportion (%)	F_d	F_p	F_h	Boiling Point (°C)	Vapor Pressure (kPa)
REF	Ethyl lactate	-	44.3	21.1	34.6	154	0.5
	Dowanol PM	-	43	20	37	119	1.56
	Isopropanol (99%)	-	38	17	45	82.4	5.2
	Ethyl lactate + ligroine + isopropanol	40–30–30	59.1	13.6	27.3	121	-
1	Acetal 1 + ethanol A.A. [1]	58–42	43.3	21.2	35.5	154.6	-
2	Acetal 1 + acetal 3	56–44	47.6	21.8	30.6	151.0	-
3	Acetal 2 + ethanol A.A.	40–60	44	19	37	81.6	-
4	Ethanol A.A.	-	35.9	20	44.1	78.0	5.73
5	Acetal 3	-	46.3	21.5	32.2	76.0	10.1
6	Acetal 2	-	56.1	17.6	26.3	87.1	17

[1] Ethanol anhydrous absolute (99%).

Based on the calculations, six solutions were selected for testing, as the ones that better reflect the reference's solubility parameters and the presumed volatility (Table 1).

The solvents were selected mainly based on their toxicological properties, according to the harmonized classification and labelling (CLP00 or ATP01) approved by the European Union (Table 2). In addition, the DNEL values (derived no- or minimum effect level for workers inhalation exposure in the acute/short terms) are provided, proving the inherent lower toxicity of the proposed solvents and solvents blends compared to the traditional ones.

Table 2. Toxicological information on the reference solvents and the proposed ones. DNEL-s: derived no- or minimum effect level—threshold for workers inhalation exposure (systemic effects—acute/short term); HC: hazard classification (CLP00; ATP01); HL: hazard labelling (CLP00; ATP01).

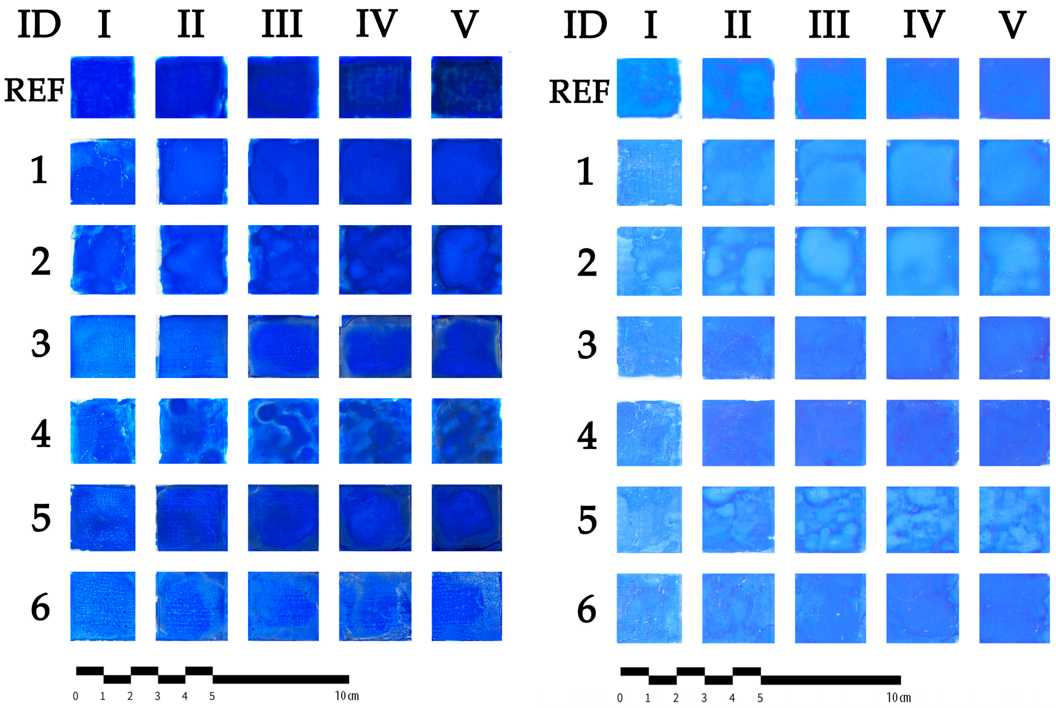
Solvent	DNEL-s (mg/m^3) *	HC *	HL *
Ethyl lactate	-	H226; H318; H335	
Dowanol PM	555.5	H226; H336	
Isopropanol (99%)	1000	H225; H319; H336	
Ligroine	1286.4	H304; H350; H340	
Ethanol A.A.	-	H225	
Acetal 1	-	-	-
Acetal 2	-	-	-
Acetal 3	-	H225	

* Data provided by ECHA (European Chemicals Agency).

2.2. Preparation of Mockups

Each solvent—the reference solvent as well—or blend was added to both the Gamblin Conservation Color and the Maimeri Restoration Color in vials in the following proportions: 4 mL of the solvent and 1.6 g of the color. The resulting mixtures were used for the gravimetric analysis and applied on prepared canvases in one to five layers, intending to evaluate the chromatic appearance and brightness of the solid color through spectocolorimetric analyses (Figure 1). The colors were applied in the same amounts using a graduated pipette and by leaving them to dry on the surface.

The prepared canvases were prepared by reproducing the real stratigraphy of a painting. The preparation layer was made with Bologna plaster and rabbit glue. Rabbit glue was added to water at a ratio of 1:16 w/v, made swell for 24 h, and heated in water bath until complete dissolution [33]. Then, sifted Bologna plaster was added until saturation of the glue. Given the yellowish color of the plaster—which might have interfered with the spectrocolorimetric analyses—a layer of white gouache (titanium white, TiO_2) was applied. Afterward, three layers of acrylic varnish were applied, based on the information obtained from the interview, using a *Lefranc&Burgeois* Superfine Retouching Varnish.



(**a**) (**b**)

Figure 1. Canvas mockups made using the Gamblin–solvents mixtures (**a**) and Maimeri–solvents mixtures (**b**) applied in one to five layers (I–V). REF: ethyl lactate; 1: acetal 1 + ethanol A.A.; 2: acetal 1 + acetal 3; 3: acetal 2 + ethanol A.A.; 4: ethanol A.A.; 5: acetal 3; 6: acetal 2.

2.3. *Gravimetric Analysis*

The proposed green solution should maintain some of the features of the more traditional organic solvents used in chromatic reintegration, not only on a chromatic level but also in terms of applicability and evaporation. Given that these properties are related to the volatility of solvents, gravimetric analysis was performed at a fixed temperature (25 °C) and relative humidity (55%) to evaluate the evaporation rate of the tested solutions. The analysis was conducted with a Kern analytical scale with a limit of four units. Three drops of each solvent-color mixture were placed on the scale's plate, measuring the weight decrease in time. The time needed by the solvent to reach a constant weight on the balance display—indicating the evaporation of the solvent from the solvent-color mixture—can be correlated to the evaporation time. The weight of the varnish color was subtracted from the calculation. Then, the results were normalized and compared.

2.4. *Spectrocolorimetric Analysis*

Spectrocolorimetric analysis was carried out on the solvent–color mixtures applied on the canvases in increasing layers to assess the one closest to the reference color, i.e., the one obtained by mixing the Gamblin Conservation Colors and Maimeri Restoration Colors with the reference solvent (ethyl lactate). The analysis was performed before and after the cleaning treatment using a portable spectrophotometer Y3060 3nh, equipped with a D65 illuminant and an 8 mm size aperture. It was carried out in the SCI mode (specular component included) and by measuring the spectra between 400 and 700 nm. The acquisitions were performed three times on each sample to reduce the uncertainty of the analysis. The data were then analyzed through the CIELab color system. Spectrocolorimetry allows one to quantitatively define color through the measurement of three parameters L*, a* and b* within the CIELab color space. L* indicates brightness, while a and b refer to chromaticity coordinates; in particular, a* goes from red ($a > 0$) to green ($a < 0$), and b* from yellow ($b > 0$) to blue ($b < 0$) [34].

Since the total color variation (ΔE*) is the most widely used parameter in the industry to define color differences, the difference between the reference layer and the one made using the proposed solvents was assessed using this parameter [23]. It is calculated as the Euclidean distance between two points through the following formula:

$$\Delta E^* = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2}$$

Values ranging from 0 to 5 are assumed as limit values, even though the average human eye can detect color changes at a ΔE around 3 or less [35–37].

2.5. Fourier-Transform Infrared Spectroscopy in Attenuated Reflectance Mode (FTIR-ATR)

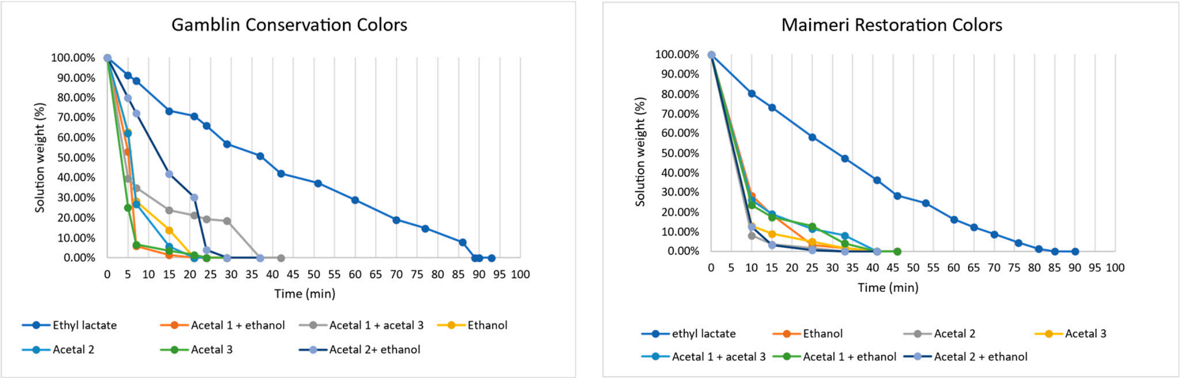
Fourier-transform infrared spectroscopy in attenuated total reflectance (FTIR-ATR) mode was used to evaluate the presence of residual solvent within the color layers. Thus, spectra were acquired on each color layer made with the proposed solvents and ethyl lactate and then compared with the spectra of the solvents. Spectra were collected after 2 h from the application using the Thermo Fisher Scientific Nicolet Summit FT-IR spectrometer and the Everest™ Diamond ATR accessory with a resolution of 4 cm^{-1} and a laser frequency of 15,798 cm^{-1}. A total of 32 scans were performed on each area. The acquired spectra were examined using the instrument library.

3. Results

3.1. Gravimetric Analysis

Ethyl lactate showed the lowest evaporation rate, corresponding to one hour and thirty minutes, which can be explained by its low vapor pressure value (0.5 kPa). For the same solvent or solvent mixture, the evaporation pattern of Gamblin Conservation Colors and Maimeri Restoration Colors is quite similar. Thus, it is possible to affirm that the difference in the composition of the two colors did not significantly affect the evaporation of the solvents.

Figure 2 shows the weight decrease in time of each solvent–color mixture. As regards the Gamblin Conservation Colors, the higher evaporation rate is given by the solution 1 (acetal 1 + ethanol A.A.) and 5 (acetal 3). Then, almost similar rates are given by solution 6 (acetal 2) and 4 (ethanol A.A.), while solutions 2 (acetal 1 + acetal 3) and 3 (acetal 2 + ethanol A.A.) show slower evaporation and more irregular trends. As regards the Maimeri Restoration Colors, the evaporation pattern of the proposed solvents is quite similar. Solutions 6 (acetal 2), 3 (acetal 2 + ethanol A.A.), and 5 (acetal 3) show the most rapid weight decrease, while the evaporation rate of solutions 1 (acetal 1 + ethanol A.A.), 2 (acetal 1 + acetal 3), and 4 (ethanol A.A.) is lower, even though similar.



(**a**) (**b**)

Figure 2. Weight decrease in time of each solvent–color mixture: (**a**) Gamblin Conservation Colors; (**b**) Maimeri Restoration Colors. The weight of the varnish color was subtracted from the calculation. The results are normalized and compared.

3.2. Spectrocolorimetric Analysis

The ΔE* values obtained from the spectrocolorimetric measurements carried out on the layers made with Maimeri Restoration Colors are shown in Table 3. It can be noted that the differences are negligible in the case of solutions 3 (acetal 2 + ethanol A.A.), 4 (ethanol A.A.), and 6 (acetal 2), showing ΔE* values smaller than 5. Solutions 1 (acetal 1 + ethanol A.A.), 2 (acetal 1 + acetal 3), and, to a lesser extent, 5 (Acteal 3) show higher ΔE* values, often reaching values of ~10. The analysis was performed in the SCI mode, which means that the changes in both lightness and gloss, together with color differences, affected the ΔE* values.

Table 3. ΔE* values obtained from the comparison between the chromatic background made with the proposed solvents and the ones made with ethyl lactate, both using Maimeri Restoration Colors: ΔE* related to the different layers and average value.

Proposed Solutions	Reference	ΔE*					
		1 Layer	2 Layers	3 Layers	4 Layers	5 Layers	Average
1 (Acetal 1 + ethanol A.A.)	Ethyl lactate	6.61	5.24	8.34	11.54	8.09	7.96
2 (Acetal 1 + acetal 3)	Ethyl lactate	5.81	6.36	12.89	11.66	11.13	9.57
3 (Acetal 2 + ethanol A.A.)	Ethyl lactate	4.98	1.73	0.93	0.85	1.46	1.99
4 (Ethanol A.A.)	Ethyl lactate	3.28	3.92	3.64	3.79	0.90	3.11
5 (Acetal 3)	Ethyl lactate	6.87	2.12	4.22	5.49	9.48	5.64
6 (Acetal 2)	Ethyl lactate	1.88	4.10	0.55	0.61	1.24	1.68

The ΔE* values obtained from the spectrocolorimetric measurements carried out on the layers made with Gamblin Conservation Colors are shown in Table 4. It can be seen that the difference between the reference layers and the ones made with the proposed solutions is greater if compared with the results obtained with the Maimeri Restoration Colors, reaching values of ~30. The only solution giving results similar to the reference is 5 (acetal 3).

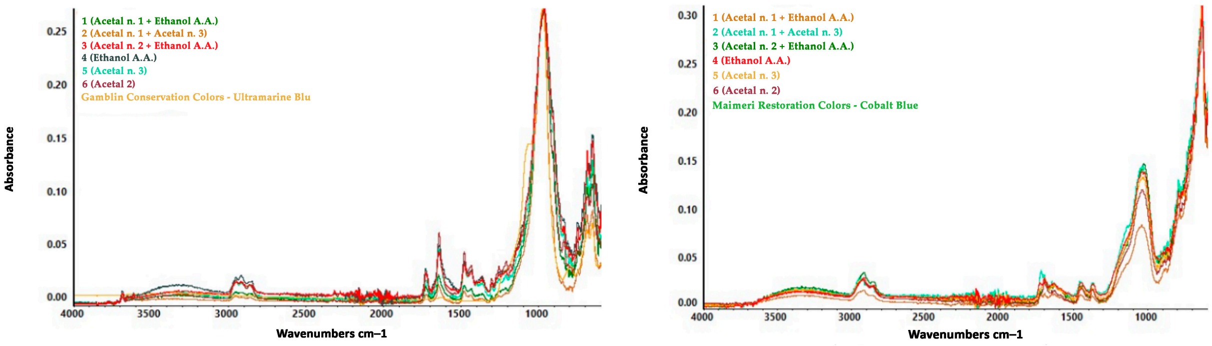
Table 4. ΔE* values obtained from the comparison between the chromatic background made with the proposed solvents and the ones made with ethyl lactate, both using Gamblin Conservation Colors: ΔE* is related to the different layers and average value.

Proposed solutions	Reference	ΔE*					
		1 Layer	2 Layers	3 Layers	4 Layers	5 Layers	Average
1 (Acetal 1 + ethanol A.A.)	Ethyl lactate	7.18	20.07	23.66	30.11	32.43	22.69
2 (Acetal 1 + acetal 3)	Ethyl lactate	8.30	17.40	31.31	25.62	31.66	22.86
3 (Acetal 2 + ethanol A.A.)	Ethyl lactate	11.29	11.31	19.88	36.26	28.64	21.48
4 (Ethanol A.A.)	Ethyl lactate	20.83	20.17	31.97	26.62	26.75	25.27
5 (Acetal 3)	Ethyl lactate	6.76	1.94	8.00	7.94	3.34	5.60
6 (Acetal 2)	Ethyl lactate	17.58	19.85	36.61	37.16	43.01	30.84

As regards the Maimeri Restoration Colors, the results of the spectrocolorimetric analyses can be summarized as follows (from the lower to the higher value): solution 6 > 3 > 4 > 5 > 1 > 2. As regards Gamblin Conservation Colors, the ΔE* values can be summarized as follows (from the lower to the higher value): solution 5 > 3 > 1 > 2 > 4 > 6.

3.3. Fourier-Transform Infrared Spectroscopy in Attenuated Reflectance Mode (FTIR-ATR)

The spectra acquired on the backgrounds realized with the proposed solvents and solvents' mixtures are reported in Figure 3. Peaks related to the presence of solvents in the dried layer—after 2 h from the application—cannot be observed. Indeed, all the solutions show the same spectrum of the Maimeri Restoration Colors and Gamblin Conservation Colors respectively, highlighting the absence of solvents' residues in the dried films.



(**a**) (**b**)

Figure 3. Spectra acquired on the dried films of color after 2 h from the application: (**a**) comparison between the spectra of the different backgrounds and the one of Gamblin Ultramarine Blue alone; (**b**) comparison between the spectra of the different backgrounds and the one of Maimeri Cobalt Blue alone.

4. Discussion

The research focused on the study of green solvents and solvents' blends based on acetals to be used as diluents for varnish colors—i.e., Gamblin Conservation Colors and Maimeri Restoration Colors—in chromatic reintegration of polychrome artworks.

Gravimetric analyses highlighted the relatively fast evaporation of the proposed solvents, since all of them showed high volatility compared to ethyl lactate, which was taken as a reference. On the one hand, high evaporation rates allow one to limit the retention of the solvent in the substrate; on the other hand, they result in a more or less opaque appearance of the color layer, since solvent evaporation, leveling, and particle diffusion all represent important factors making the painted surface vary during the drying process [38]. Medium-high evaporation rates might therefore be useful when a slightly opaque surface is desired. FTIR-ATR analysis did not highlight the presence of solvent residues inside all the backgrounds, regardless of the number of superimposed layers, confirming the complete evaporation of all solvents not being retained by the substrate.

As regards the Gamblin Conservation Colors, the results of the analytical process show that solution 5 (acetal 3) and, to a lesser extent, solution 1 (acetal 1 + ethanol A.A.) represent the most suitable alternatives to traditional solvents. Acetal 3 is the only solvent that shows a similar F_d value and negligible color variations if compared with the backgrounds made using ethyl lactate, even though its boiling temperature and the vapor pressure are respectively lower and higher that the ones of the reference solvent. Acetal 1 + ethanol A.A. shows almost the same evaporation rate as acetal 3, although its boiling temperature is similar to that of ethyl lactate and its supposed vapor pressure should be lower than the one of acetal 3. The apparent contradiction presented by the results can be explained by the specific interaction among the solvents or the solvents' blends and the color's constituents affecting the evaporation process.

As regards the Maimeri Restoration Colors, the ΔE^* calculated for the applications made with solutions 3 (acetal 2 + ethanol A.A.), 4 (ethanol A.A.), and 6 (acetal 2) fall within the accepted range. Solution 6 (acetal 2), together with solution 3 (acetal 2 + ethanol A.A.), has the highest evaporation rate, even though all the solvents show almost the same pattern when used in combination with the Maimeri Restoration Colors. It has an F_d value of 56.1, which is similar to the 40-30-30 mixture of ethyl lactate, ligroine, and isopropanol (F_d = 59.1). Thus, it may be considered a relatively highly volatile alternative to this blend. Solution 3 (acetal 2 + ethanol A.A.) represents a suitable volatile solution as well since the F_d value (44) is similar to the that of ethyl lactate (44.3), and dowanol PM (43). Ethanol A.A. alone appears to have good optical properties and a medium-high evaporation rate. However, its F_d value makes the other two solutions preferable.

5. Conclusions

Finding a green solvent able to maintain the same effect as traditional solvents in terms of spread, applicability, removability, and volatility is challenging. Many aspects must be taken into consideration, from the physical–chemical parameters and the threshold limit values to the desired final effect. Potential alternative solvents need to be tested and validated by restorers to understand the actual functionality, application methodology, and operational defects.

The study enabled the identification of suitable green acetal-based formulations to be used as diluents with Maimeri Restoration Colors and Gamblin Conservation Colors. Acetals are organic solvents based on a $R_2C(OR')_2$ structure. They are bioderived and safer for the operator and the environment if compared to more traditional solvents, as confirmed by harmonized classification and labelling (CLP00 or ATP01) and toxicological data.

The solvents–color mixtures confirmed that acetals or mixtures of acetals and alcohols can solubilize both the synthetic resin Laropal® A81, which is the binder of Gamblin Conservation Colors, and the terpene resin mastic, i.e., the binder of Maimeri Restoration Colors. The results obtained from the whole analytical process show that acetals or acetals–ethanol blends can be excellent medium-high volatile alternatives to more traditional solvents that are commonly used for the dilution of the tested varnish colors.

Specifically, acetal 3 appears to be better suited for Gamblin Conservation Colors, while acetal 2 and the mixture of acetal 2 (40%) and 60% ethanol A.A. (60%) seem to be the most appropriate for the dilution of Maimeri Restoration Colors.

Future research could focus on controlling the volatility of the proposed solvents and solvents' blends, either by using surfactants, modifying the percentages of the proposed mixtures, or creating ternary mixtures solvents having lower volatility. The evaporation rate of the blends that provided the best results in this study could be modulated to maintain the desired optical properties. In addition, the future aim of the experiment is to provide restorers with the solvent mixtures which gave the best results in this study in order to verify their applicability and orientate future research in modulating blends' volatility.

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