Material Analysis for Temple Painting Conservation in Taiwan

Chen-Fu Wang, Lin-Ya Kung

Abstract-For traditional painting materials, the artisan used to combine the pigments with different binders to create colors. As time goes by, the materials used for painting evolved from natural to chemical materials. The vast variety of ingredients used in chemical materials has complicated restoration work; it makes conservation work more difficult. Conservation work also becomes harder when the materials cannot be easily identified; therefore, it is essential that we take a more scientific approach to assist in conservation work. Paintings materials are high molecular weight polymer, and their analysis is very complicated as well other contamination such as smoke and dirt can also interfere with the analysis of the material. The current methods of composition analysis of painting materials include Fourier transform infrared spectroscopy (FT-IR), mass spectrometer, Raman spectroscopy, X-ray diffraction spectroscopy (XRD), each of which has its own limitation. In this study, FT-IR was used to analyze the components of the paint coating. We have taken the most commonly seen materials as samples and deteriorated it. The aged information was then used for the database to exam the temple painting materials. By observing the FT-IR changes over time, we can tell all of the painting materials will be deteriorated by the UV light, but only the speed of its degradation had some difference. From the deterioration experiment, the acrylic resin resists better than the others. After collecting the painting materials aging information on FT-IR, we performed some test on the paintings on the temples. It was found that most of the artisan used tune-oil for painting materials, and some other paintings used chemical materials. This method is now working successfully on identifying the painting materials. However, the method is destructive and high cost. In the future, we will work on the how to know the painting materials more efficiently.

Keywords—Temple painting, painting material, conservation, FT-IR.

I. INTRODUCTION

TRADITIONAL architectural paintings consist of three parts: the basement layer, the earthly layer, and the painted layer. The base material is mostly wood, gray wall and stone. The earthly layer is linseed oil, blood, and linen [1]. Painted layer is pigments and binders (Tung-oil or linseed oil) and other materials. The painted layer is considered to be the essence in architecture. But due to the exposure to sunlight, moisture, dust, and contaminants, the painted layer being most exposed is also first to deteriorate in architecture. Therefore, during the repair process, the restoration of the painted layers is essential to bring back beauty of the architecture. In recent years, the relevant architectural painting research has begun to use scientific

instruments including thermogravimetric analyzer and fluorescent analyzer to detect lime and paint materials. But there is no standard system for painting material analysis. Most of the current painting repair work is relied heavily on artisan's experience to decide the materials to be used.

In order to take a scientific approach in restoration, it is necessary to categorize and analyze different types of materials, production process, and how each material age and deteriorate. Through establishing the database, it can allow a more systemic approach in restoration.

II. HISTORY REVIEW

The painting materials can be divided into two parts, pigment and binders. Over the years, painting materials have evolved through changes in manufacturing process and obtaining method. Traditional architectural painting of Taiwan have a great variety, the relevant materials are as follows:

A. Pigments

The main pigment is mineral-based inorganic pigments, including red, chrome yellow, green, blue, Zhou, and white, the other colors are mixed by the main colors [2].

With the development of chemical industry, new inexpensive and more available materials gradually replace the old materials. Modern organic pigments due to the color, is brighter than the traditional painting inorganic pigment. It has replaced most of the traditional painting materials.

The modern painting made is through artisan mixing the binder and color toner to form the base liquid color paint that does not fade. The linen oil is then added into the base paint to form the coating material. The original color paint has become widely used for its convenience of not needing to polish toner particles, boiling Tung oil, and other steps. In addition, the modern paint color types are more vibrant and availed in more colors.

B. Binders

The traditional binder is mainly Tung oil and linseed oil [3]. Tung oil can be divided into raw Tung oil and cooked Tung oil. Cooked Tung oil is mainly used for the first layer of paint or making color toner. It can also be used as a painting coating after the completion of the painting.

In the past, the cooked Tung oil is cooked by each artisan and everyone had their own secret recipe. In general, if the color toner is made from raw tune oil, it does not dry as easily as cooked Tung oil. At present, the Tung oil used by the artisan is mostly made by the paint factory (see TABLE I). Some factories can even modulate the Tung oil with different orders. As the same time, the function of Tung oil as a protective

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coating is replaced by the bright lacquer which is made by the factory. Linseed oil is used to control the drying speed the stickiness of the color, in the current time, the linseed oil is all made by the factory. Decorative gold foil, copper foil is achieved by pasting gold/copper oil to the paint surface. Traditional artisan often used tree sap, with some cooked Tung oil mixing with raw ting oil to make the binder. The modern way of applying gold foil is by using the bonder made by factory which is chemical materials which is yellow in color and adhesive.

Modern artisans in addition to use Tung oil, linseed oil which are made by factory, other materials are also used, such as vegetable-oils and modern chemical synthetic resins, including Soybean oil, castor oil, urushiol, walnut oil, sunflower oil, poppy oil, fish oil and other natural oils and fat, and modern synthetic acrylic resin, alkyd resin coating, polyurethane coating (PU).

TABLE I THE PAINTING MATERIALS IN TAIWAN [4]

Building	Age	Material	Artisan						
Tainan da tian hougong	1920	Pigments + linseed oil + Tung oil	Chényùfēng						
Tainan beiji dian	1969	Color toner + linseed oil	Càimùwén						
Taipei wanhua longshansi		Pigments + linseed oil + tung oil	Chénshòuyí						
Tainan da tian hougong	1980	Color toner + linseed oil	Dīngqīngshí, Cáo tiānzhù, Liújiāzhèng						
Tainan tiantan	1984	Color toner + linseed oil	Càimùwén						
Tainan sanshan temple	1995	Color toner + linseed oil	Càimùwén						
Tainan wu temple	1996	Color toner + linseed oil	Cáoxianwén						
Taipei wanhua longshansi	1997	Color toner + linseed oil	Càilóngjìn						
Tainan chikanlou	1997	Color toner + linseed oil	Cáo tiānzhù						
Tainan da tian hougong	1998	Color toner + linseed oil	Càimùwén						
Tainan jin tang dian	1998	Color toner + linseed oil	Chéntiānxiáng						
Zhanghua Jinmen	1999	Color toner + linseed oil	Pānyuè xióng						
guan		Color toner + linseed oil	Chénshòuyí						
Tainan chenhuang temple	2000	Color toner + linseed oil	Càimùwén						
Tainan kaiyuan temple	2000	Color toner + linseed oil	Càimùwén						
Tainan zhen xing temple	2001	Pigments + Tung oil	Chén dūnrén						
Taipei wu temple	2002	Color toner +linseed oil	Càilóngjìn						
Taipei bao an temple	2002	Color toner +linseed oil	Pānyuè xióng						
Taichung huang xi shuyuan	2002	Pigments +Tung oil	Chén dūnrén						

III. RESEARCH METHODS

This research is based on the conditions of the known painting materials in current repair work and restoration work. After collecting the painting materials, we use FTIR to record the data, and we also use colorimeter to record the change of the color. The principal component analysis (PCA) method is then used to analyze the results of the aging test.

A. Samples

A total of nine types of binders were tested, including NC lacquer, PU, cashew, urushiol, nitrocellulose, acrylate, shellac,

Tung oil and linseed oil. As the characteristics of each material are not the same, the production of test pieces will be the difference between the characteristics of the binders.

By adding the appropriate solvent, and the use of simple viscosity cup to adjust the viscosity to 15 seconds, then coated with a film on the glass test piece, the size of the glass test piece is 10×15 cm, the film thickness is 200 µm, and the dried at room temperature.

B. Aging Time

After the test pieces are dried, we put them into the paint coating fade meter machine. And start to run the aging test. Test tank temperature is 30 ± 4 °C, the light source for the H400-F mercury lamp, and analysis the test piece by 0hr, 100hr, 500hr, 1000hr, and then doing the colorimeter test.

C. Colorimeter Analysis

In the research, we use Minolta (CM-3600d, Japan) for identifying color differences. Follow the CIE to calculate the color differences. The calculate formula is as below:

$$\Delta L^* = L^* t -$$
(1)

$$\Delta a^* = a^* t - a^* 0 \tag{2}$$

$$\Delta b^* = b^* t - b^* 0 \tag{3}$$

$$\Delta E^{*}=[(L^{*}t-L^{*}0)2+(a^{*}t-a^{*}0)2+(b^{*}t-b^{*}0)2]1/2$$
 (4)

$$\Delta YI = YIt - YI0 \tag{5}$$

IV. RESULT

A. Color Difference

The results of the color change of the samples are shown in Table II. ΔL * shows the difference in lightness and darkness. It is negative values for binders, NC lacquer, PU, cashew, acrylic, nitrocellulose and linseed oil. It decreases with the increase of the aging time. Indicating that the coating has a tendency to darken. And binder lacquer, shellac, and Tung oil, the ΔL * are all positive with the increasing in light, it indicated that the coating has a whitening phenomenon. And lacquer's ΔL * increase the most obvious from 100hr to 1000hr; it is respectively, 29.84 and 35.30.

 \triangle a * shows the difference in red and green. Most of the binders show the increase with the aging time. Only lacquer and shellac is opposite. (\triangle b *) shows the difference in yellow and blue, it is similar to \triangle a *. On the whole, \triangle a * and \triangle b * changes in nitrocellulose, acrylic resin, Tung oil and linseed oil is less obvious.

 ΔE *shows the total color difference, in addition to lacquer, the other binders are increased with aging time. The ΔE *of binder nitrocellulose, acrylate, and linseed oil is less than 1.5; the naked eye cannot clearly identify the difference in color changes. ΔE * changes more obvious on binder PU, lacquer, and shellac. There may be because the composition contains more benzene ring structure, and benzene ring structure is easy to light and photo-oxidation reaction, resulting in degradation

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of the coating surface composition.

TABLE II										
COLOR DIFFERENCE DATA										
Binder	Hours	∆L*	∆a*	∆b	∆E*	∆YI*				
		-0.37	-0.70	2.40	2.53	4.98				
	100	(0.04)	(0.02)	(0.04)	(0.04)	(0.08)				
N.C		-0.95	-0.78	3.28	3.51	6.91				
lacquer	500	(0.21)	(0.03)	(0.10)	(0.05)	(0.30)				
		-1.17	-0.96	4.25	4.51	9.02				
	1000	(0.10)	(0.03)	(0.05)	(0.05)	(0.10)				
		-4.81	-1.36	17.97	18.66	38 70				
	100 500	(0.09)	(0.32)	(0.36)	(0.35)	(0.75)				
PU		-6.40	-0.97	23 57	24 44	50.17				
		(0, 08)	(0.09)	(0.53)	(0.57)	(1 12)				
	1000	-7.10	-0.74	27.12	28.04	57.14				
		(0.23)	(0.11)	(0, 70)	(0.73)	(1 41)				
Cashew	100 500	(0.23)	0.21	2.26	2 32	(1.41)				
		(0.13)	(0.23)	(0.47)	(0.46)	(0.81)				
		0.82	0.20	2 75	2.80	5.42				
		(0.22)	(0.22)	(0.38)	(0.40)	(0.70)				
		1 22	0.42	2 20	2 55	(0.70)				
	1000	(0.17)	(0.42)	(0.22)	(0.20)	(0.35)				
		20.84	(0.22)	(0.23)	(0.20)	(0.33)				
	100	29.04	(1.00)	40.71	(0.02)	-25.42				
		24.02	(1.99)	28.61	(0.93)	(14.40)				
Urushiol	500	34.92 (0.77)	4.50	58.01	52.27	-44.50				
		(0.77)	(2.14)	(0.42)	(0.09)	(14./4)				
	1000	35.30	3.30	32.88	48.04	-53.80				
		(0.81)	(1.29)	(0.61)	(0.57)	(14.09)				
	100	-0.23	-0.02	0.44	0.50	1.00				
		(0.10)	(0.01)	(0.04)	(0.08)	(0.10)				
nitrocellu	500	-1.07	-0.08	1.22	1.64	2.70				
lose	1000	(0.48)	(0.03)	(0.21)	(0.46)	(0.43)				
		-1.11	-0.05	1.22	1.66	2.72				
		(0.47)	(0.01)	(0.15)	(0.41)	(0.28)				
	100	-0.11	0.10	0.33	0.39	0.78				
		(0.05)	(0.17)	(0.01)	(0.05)	(0.03)				
Acrylate	500	-0.29	0.12	0.44	0.56	1.05				
		(0.08)	(0.17)	(0.06)	(0.12)	(0.13)				
	1000	-0.36	0.04	0.36	0.53	0.73				
		(0.07)	(0.17)	(0.07)	(0.10)	(0.17)				
	100	3.99	0.19	-9.29	10.11	-18.51				
Shellac 50		(0.08)	(0.03)	(0.23)	(0.22)	(0.35)				
	500	5.66	-0.44	-17.51	18.41	-36.54				
		(0.12)	(0.02)	(0.35)	(0.37)	(0.61)				
	1000	7.51	-1.36	-24.64	25.79	-53.76				
		(0.11)	(0.01)	(0.39)	(0.39)	(0.70)				
Tune oil 4 1 Linseed 4 oil 1	100	0.86	0.03	0.31	2.74	0.99				
	100	(0.01)	(0.01)	(0.02)	(0.01)	(0.04)				
	500	3.80	0.29	-0.37	11.48	0.19				
	500	(0.27)	(0.02)	(0.08)	(0.28)	(0.16)				
	1000	6.35	0.39	-1.35	19.50	-1.66				
		(0.20)	(0.01)	(0.07)	(0.21)	(0.13)				
	100	-0.26	-0.03	0.64	0.69	1.47				
		(0.08)	(0.01)	(0.03)	(0.05)	(0.06)				
	500	-0.42	0.02	0.41	0.59	0.93				
		(0.08)	(0.01)	(0.02)	(0.07)	(0.06)				
	1000	-0.65	-0.03	0.29	0.71	0.54				
		(0.17)	(0.01)	(0.09)	(0.19)	(0.19)				

The difference in yellowness (\triangle YI) is mainly calculated by the influence of \triangle a * and \triangle b *. With the change of aging time, the \triangle YI of the binders will increase, lacquer and shellac are in opposite situation. While nitrocellulose, acrylic, Tung oil, and linseed oil are less obvious.

B. FT-IR Analysis

In recent years, due to the progress of analytical technology, seeking a quick and easy classification method has become very important. In the past, studies have shown that different types of wood cells can be discerned by FT-IR [5]. PCA analysis also can be used to distinguish between plastic and recycled plastic. In this experiment, the spectra of known materials were established by FT-IR, and it was clustered by PCA as a reference for the future spectral placement of unknown coatings, and to speculate on the basis of the possible composition of the unknown coating.

1. NC Lacquer

From Fig. 1, with 1000 hours aging time, the spectra at 1650 cm^{-1} , 1280 cm^{-1} and 840 cm^{-1} still have obvious absorption intensity.



Fig. 1 FT-IR spectra of NC lacquer with different aging time

2. PU

From Fig. 2, with 1000 hours aging time, absorption peak intensity at 1720 cm^{-1} and 3350 cm^{-1} widens with the aging time.

3. Cashew

Fig. 3 shows the change of ATR-FTIR pattern after aging t times. The intensity of absorption peak is obviously to see at 2925 cm^{-1} and 2855 cm^{-1} .



Fig. 2 FT-IR spectra of PU with different aging time

4. Urushiol

Fig. 4 shows the change of ATR-FTIR pattern after aging time, which decreases with the increase aging time, while 1730 cm^{-1} is the structure of C = O, and the intensity increases with

7. Shellac

the increase of aging time.



Fig. 3 FT-IR spectra of Cashew with different aging time



Fig. 4 FT-IR spectra of urushi with different aging time

5. Nitrocellulose

In Fig. 5, the intensity of the characteristic absorption peak decreases with the increase aging time.



Fig. 5 FT-IR spectra of nitrocellulose with different aging time

6. Acrylate

In Fig. 6, even after 1000 hours aging time, the intensity of the absorption peak did not change much.

In Fig. 7, after 1000 hours aging time, the intensity of the absorption peak is less obvious at 1250 cm^{-1} and 1045 cm^{-1} .



Fig. 6 FT-IR spectra of acrylate with different aging time



Fig. 7 FT-IR spectra of shellac with different aging time

h. Tung Oil and Linseed Oil

In Fig. 8 and Fig. 9, they have the same absorption spectra of 2925 cm⁻¹, 2855 cm⁻¹, 1450 cm⁻¹, 725 cm⁻¹, and it all less obvious after 1000 hours aging time.



Fig. 8 FT-IR spectra of Tung oil with different aging time

C. PCA Analysis on Defining Different Materials

In Fig. 10, it shows the results of PCA analysis of nine binders. It can be seen that PC1 can explain the variation of

50.51% and PC2 34.58%. PC1 is mapped to PC2, which can explain 85.09% variation.

It can be seen from Fig. 10, that PC1 can distinguish nitrocellulose from the nitrocellulose as the main component, and the PC1 fraction of the two components is negative. PC2 can distinguish PU from others, and the PC2 fraction is positive. But not as expected, cashew, urushiol, acrylic, shellac, Tung oil, and linseed oil distinction is not very obvious.



Fig. 9 FT-IR spectra of linseed oil with different aging time

■NC lacqer ◆PU ▲Cashew ◇nitrocellulose ◇Arylate △Sellac ○Tng oil * Linseed oil



Fig. 10 0 hours PC1 Score on PC2 Score

In Fig. 11, it shows the results of the PCA analysis of the binders after 100 hours aging. From the figure, it can be seen that PC1 can explain the variation of 58.36% and PC2 20.24%. PC1 is plotted on PC1, which can explain 78.60%. Compared with the 0hour PCA results can also be significantly differentiated nitrocellulose and NC lacquer, while after 100hours, the PU and cashew can be distinguished by PC1 and PC2 clearer.

In Fig. 12, it shows the results of PCA analysis for nine binders for 1000 hours aging. The PC1 analysis is similar to the case of aging time 0 and 100 hours, which clearly distinguishes between nitrocellulose and NC lacquer. And PC1 is negative.

V.CONCLUSIONS AND RECOMMENDATIONS

Based on the above results, it was found that any natural or synthetic polymer compound was deteriorated by the influence of ultraviolet light, only its deterioration speed and degree of difference, in which the acrylic resin is better lightfastness. ■NC lacqer ◆PU ▲Cashew ◇nitrocellulose ◇Arylate △Sellac ○ Tng oil * Linseed oil



Fig. 11 100hours PC1 Score on PC2 Score

■NC lacqer •PU ▲Cashew onitrocellulose oArylate △Sellac OTng oil * Linseed oil



Fig. 12 1000hours PC1 Score on PC2 Score

The use of PCA can clearly separate nitrocellulose, PU, cashew, and acrylic. But the Tung oil, linseed Oil, urushiol, cashew, and shellac is still not easy to distinguish.

In the future, we may focus on the non-destructive method, to identify the binders, and use the method to work on the conservation work and repair work examination.

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