Reconstruction of the Historical Golden Pigment Making Process Based on BnF Ms. Fr. 640

Abstract

Historical pigments are of great importance in the modern world due to their aesthetic qualities and potential uses. However, nowadays, instead of following the recipes found in historical manuscripts that artists in the past once used, market-made historical pigments are made out of organic chemicals that mimic the character of historical pigments. The problem is it is not clear if these market-made pigments actually recreate the true character of the ancient pigment. In this research, we reconstruct the historical golden pigment-making process based on the sixteenth-century artisanal manuscript BnF Ms. Fr 640, f. 76v and f. 104r, and compare the manuscript-based historical pigments against the market historical pigment, by doing spectrophotometry test, pH test, RGB test, and light fastness test. The result is fascinating: on the one hand, this project allows future researchers to produce the pigment described in this recipe, while on the other hand, it raises an interesting question about how authentic market-made pigments are.

Introduction

I. Defining terms

Before considering the value of the primary task of this research, which is to reconstruct a pigment based on a historical manuscript, some terms should be defined to delineate the problem. In the history of Western painting since the Renaissance, there are two major categories of pigments:

Historical pigments: 19th-century colors of Impressionists and the colors of the Classical and Renaissance era

Modern pigments: Colors after the 20th century when synthetic colorants were used to produce colors that were formerly derived from natural means.

Within the subsection of historical pigments we have two further subdivisions:

Market "historical" pigments: Colors where scientists used organic chemicals to mimic the characteristics of historical pigment.

Manuscript-based historical pigments: Colors made by following the exact historical manuscript, usually made out of plants and minerals.

II. The Importance of Historical Pigment

First, contemporary artists express a need for historical pigments because of their aesthetic qualities and potential uses. Modern pigments and historical pigments behave differently in color mixing. For example, below are two different colors, the mineral Cadmium Red Medium and modern Naphthol Red, each mixed with Titanium-Zinc White.

Figure.1 The mineral Cadmium Red Medium mixes with Titanium Zinc White (Left)
Modern Naphthol Red mixes with Titanium Zinc White (Right)

As shown above, Cadmium Red Medium loses its intensity when mixed with Titanium-Zinc white while Modern Naphthol Red keeps its intensity. This difference holds for any historical pigments vs. modern pigments. Historical pigments shift in value and Chroma, while modern pigments shift only in value (Gamblin Colors 2019). Therefore, for a special group of artists, who intend to capture the color of the natural world and imitating the effect of natural light, modern pigments would be too strong for them. Also, modern pigments would overlap each other and cannot give the ideal effect. For example, Mr. Feng Hai Tao, a famous Chinese artist, once said, "all I used were colors of the minerals. I did not use synthetic color in my painting." (Feng 2018)

Moreover, a need for the use of the traditional method to produce pigments is inevitable for conservators. Italian archeologist Anna Hartl led the research on looking for a blue pigment with wood fermentation vats to fulfill the need of reproducing an Iron Age textile (Hartl 2015). Thus, we can recognize a need for historical pigments in the contemporary world.

III. Market "historical" pigments vs. Manuscript-based historical pigment

Currently, there are several kinds of historical pigments for sale on the market, and they intend to use organic chemicals to mimic the characteristics of historical pigment. However, the problem with this method is we can only mimic what we know. It is not clear if these market-made pigments actually recreate the true character of the ancient pigment unless we, as scientists and artisan, make the ancient pigment ourselves based on the ancient manuscript.

IV. Challenges of reconstructing a pigment based on a manuscript

The traditional approach is based on a manuscript, BnF. Ms. Fr 640, written in 16th century France. The manuscript was written by an experienced practitioner. The manuscript constitutes the written record of the author-practitioner's collection of recipes and his own investigation, covering a wide range of topics, including pigment making, metal casting, and hilariously, even dog taming. However, different from a scientific handbook, the manuscript's lack of formulaic recipes, constant reference to practitioner's own experience and numerous annotations in the margin, make the manuscript more like a set of working notes rather than a followable instruction (Smith 2004). In other words, the procedure in this manuscript is not designed to be reproduced by the act of solely "reading through", but rather through an act of imitation and investigation similar to what the practitioner did himself.

V. Research Question

Why for some paintings the modern replica looks different from the original one? Although the modern replica might get the shape right, it still lacks a certain "feeling". What would contribute to this nuance? Is there a difference between market-historical pigment and manuscript-based historical pigment? If so, what are the key differences between the two kinds of historical pigments, taking golden pigments as an example specifically?

VI. Hypothesis

My hypothesis is that this subtle difference comes from the pigments they use. Historical pigments were extracted from the minerals or plants. However, nowadays the market-made pigments are made out of organic chemicals that mimic the character of historical pigments. Comparing the market-historical golden pigment with the manuscript-based historical pigment might have different pH value, mixture components, RGB value and light retention time, for example.

VII. Goals

Reconstruct the historical golden pigment-making process based on BnF Ms Fr 640 f. 76v and f. 104r. Compare the manuscript-based historical pigments against the market historical pigment, by doing pH test, TLC test, photographic documentation and light fastness test. After my project, it would be easier for others to follow this procedure. More people would thus regain knowledge of recreating the historical process of pigment making as well as the characteristics of these pigments.

Procedure

First, choose the desired recipe from the manuscript. Read the recipes and fill in the missing parts with reasonable deduction. Then, transform the qualitative recipe into a quantitative experimental procedure (see Attachment for detailed 76v and 104r experimental procedure). Finally, compare two Manuscript- Based Golden Pigments (76v, 104r) with the Market Historical Pigment using scientific description and opinion- based description.

Read the manuscript and fill in the missing part with reasonable deduction

In BnF Ms Fr 640 manuscript, the author practitioner mentioned two recipes to make the golden pigment: f. 76v and f. 104r. In f. 76v, he recorded a way "to make a very beautiful and inexpensive golden color", and in f. 104r, he mentioned how to make a "good mixture to color gold".

A. 76v: to make a very beautiful and inexpensive golden color

1. As instructed by the author practitioner, the first step is to "take a very yellow-orange peel and carefully remove the white parts". In fact, the practitioner did not mention the type of orange to use. In order to best mimic the historical condition, we decide to use Navel Sunkist, a type of orange originated in France.
2. Then, according to the manuscript, the orange peel is supposed to " [be] pulverized well in a clean mortar". However, large pieces of orange peel are slippery and hard to pulverize. Instead of being directly pulverized, the orange peel is first to cut into smaller pieces. Then use a smasher to crush the orange peel pieces into powders. If there are still noticeable big particles, use the mortar to pulverize the big particles into very fine powders.
3. The next step recorded in the manuscript is to "take the same amount of sulfur, grind all the ingredients together." Still, when referring to "take the same amount," the author practitioner did not mention whether they do it by weight or volume. Notwithstanding, assuming there was no accessible way to measure the volume in a 16th-century artisan workshop, we believe those artisans measure the ingredients by weight.
4. Then, the author practitioner says to pour the mixture into "a glass vial". The question occurs when deciding whether to seal the glass vial or not. Several choices seem possible: to completely seal the glass vial, to seal the glass vial while leaving some air holes, and to completely leave the glass vial open. Therefore, we plan to do a control experiment based on different ways of sealing.
5. Finally, according to the recipe, the glass vial is stored in a "cellar or other damp place" for eight or ten days. Obviously, the damp place is not an accurate word to describe a storage environment. Looking up the information about the 16-century cellar, we suppose the modern

equivalent for the cellar is a thermostable environment with high humidity. To better control the environment, we decide to make a closed engineering box to mimic the cellar system.

B. 104r: A good mixture to color gold
   1. The second manuscript seems to be a much more simple recipe than 76v that it neither requires the sophisticated storing environment nor the time-consuming fermentation process.
   2. The manuscript simply says to take “sulfur and small gravel as much of one as of the other, and the third part of this quantity of salt, and as much turmeric as sulfur”. Although the syntax is complex, we interpret it as taking the same amount of sulfur, salt, and turmeric, mixing them together, and using gravel to pulverize them into powder. However, as we already get the fine powder of sulfur, salt, and turmeric, in this case, the use of gravel is not necessary, which make the whole process even easier to proceed.

Overall, 76v focuses on using orange peel and sulfur to make the golden color, while 104r focuses on using turmeric, salt, and sulfur. An interesting fact is that both of the recipes mention the use of sulfur, making us interested in the role of sulfur in pigment making.

Transform the qualitative manuscript into a quantitative experimental procedure

A. 76v: to make a very beautiful and inexpensive golden color
   1. Experimental Material
      a) Three medium-size Sunkist Navel Orange, 3g sulfur, two mortars, a knife, a smasher, a timer, a 10’12’8’ plastic box, a thermometer, a hygrometer, a humidifier, a refrigerator, and several pieces of tissue papers are used in this experiment.

   2. Experimental Process
      a) Prepare Orange Peel Powder
         (1) Wear gloves and goggles during the experiment process, because sulfur is poisonous. Put several tissue papers on the lab table, in case the orange oil contaminate the lab equipment.
         (2) First of all, peel off three orange’s peel using a knife. Be careful to not to peel off the white part.
         (3) Then, cut the orange peel into smaller pieces.
         (4) Insert the orange peel pieces into the smasher. Use the smasher to crush the orange pieces into particles and collected them in the mortar. Pay extra attention to the extracted orange oil, which might be helpful to serve as a binder for further pulverization.
         (5) Pulverize the orange peel particles for at least 5 mins until they turn into very fine powders.
      b) Prepare Orange Peel Sulfur Mixture
         (1) Take 1g orange peel from the finished pulverized orange peel powder, and put it in another clean mortar.
         (2) Measure 1g sulfur powder, and add it into the mortar with orange peel powder.
         (3) Pulverize the orange-sulfur mixture for at least another 5mins, until it’s hard to distinguish between sulfur powder and orange peel powder.

(4) Pour the orange peel-sulfur mixture to a petri dish.
(5) Repeat step (a) to (d) for two more times, which ends up with three Petri dishes each contains 2g orange peel sulfur mixture.

c) Seal the Petri Dish
(1) Three Petri dishes are sealed differently. The first petri dish is completely sealed by the plastic wrap and is labeled as the air-tight group.
(2) The second petri dish is sealed by the plastic wrap as well, but is poked with some air hole, and is labeled as the air-flow group.
(3) The third petri dish is completely open, leaving contact with air freely, and is labeled as the air-free group.

d) Build the Cellar Environment
(1) Put the humidifier at the center of the box, and put the three Petri dishes into three corners of the box, to ensure they are from the same distance to the central humidifier.
(2) Tape the thermometer and hydrometer to monitor the interior temperature and humidity.
(3) Place the box inside the refrigerator, and adjust the temperature to 10 degree Celsius, the cellar temperature in the 16th century.
(4) Check the temperature and humidity every day, add water to the humidifier if needed.

3. Experimental Clean Up: After 10 days, take the box out of the fridge and get the three samples of the golden pigment.

B. 104r: A good mixture to color gold
1. Experimental Material: 1g sulfur, 1g turmeric, 1g sodium chloride, and mortar are used in this experiment.
2. Experimental Process
a) Wear gloves and goggles during the experiment process, because sulfur is poisonous. Weight 1g of sulfur, turmeric and sodium chloride.
b) Pour the mixture into a clean mortar, and pulverize them for at least three mins until they turn into fine powders.

C. Apply the self-made pigment
1. Mix 1g self-made golden pigment with 1g gum arabica, a common use medium for watercolor.
2. Repeat this process four times, each with air-tight 76v, air-flow 76v, air-free 76v, and 104r.

Data Analysis

We compare the self-made-historical golden watercolor pigment against the market-modern golden watercolor pigment and market-historical golden watercolor pigment. The reason we choose watercolor is to control the medium that the market watercolor still uses gum arabica as its medium. Therefore, we need to characterize four samples: market-modern pigment, market-historical pigment, 76v pigment, and 104r pigment.

Scientific Describe

A. pH Test
   1. Calibrated the pH meter.
   2. Awaiting the pH reading to settle down, take the reading of the sample.
   3. Repeat this process and record the pH reading for the other three sample accordingly.
B. Spectrometry Test
   1. Testify the absorbance of each sample in different wavelength.
   2. Record the absorbance and draw its characteristic graph (transmittance vs. wavelength).
C. Apply the pigment on the desired surface
   1. Apply the four sample pigments on paper, canvas, and plywood board in sequence.

D. RGB Color Test
   1. Document the sample photographically with a color reference chart and characterize the color using the National Color System Code under standardized light.
E. Lightfastness Test
   1. Access with a standard Xenon test to testify the retention time based on Blue Wool rating.

Subjective Describe

Considering art is a subjective area, we incorporate a subjective description by asking professional artists and conservators to evaluate the artistic values of each sample.

Results & Discussions

As shown below, in the reconstruction process of fol. 76v, among the three methods of pulverizing orange peel, using micro blade resulted the most uniform powder; among two environment with different humidity, the one with higher humidity resulted the most homogenous color. Therefore, we concluded smaller particles and higher humidity can resulted the best color when applying recipe for. 76v.

Table 1. The Resulted Color Comparison Between Three Methods of Pulverizing Orange Peel

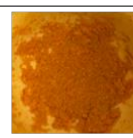
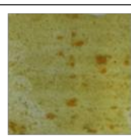
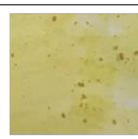
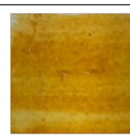
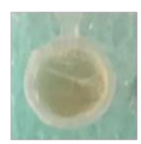
Tools			
Orange peel powder			
Resulted Color			

Table 2. The Resulted Color Comparison Between Different Humidity

Situation		
Humidity	50RH	80RH
Temperature	12°C	12°C
Resulted Color		

As shown in *Figure. 6,* in the spectrometry graph, The general trend of transmittance for Market Historical Pigments and Manuscript Based Historical Pigments is similar: the Transmittance increase as the wavelength increase. However, Manuscript Based Historical Pigments have a flatter distribution in 450-850 wavelength, while Market Historical Pigment is gradually increasing. Therefore, it shows two Manuscript Based Historical Pigments have a different color compare to the Market version. After we apply the color to the standard 300 GSM water color paper, we analysis the RGB value of each color. In RGB test, the R value for three pigments are similar, all around 200. But Manuscript Based Historical Pigments have a higher G value in RGB Test. Again, it proves the difference between the color from different methods.

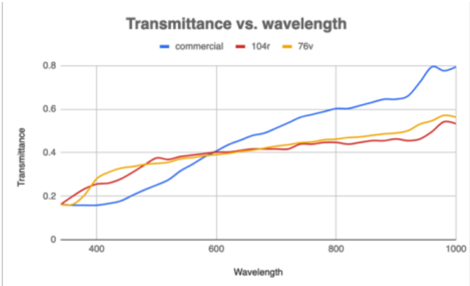


Figure 6. Spectrophotometry graph of Transmittance vs. Wavelength (For f. 76v and f. 104r were Adjusted by Concentration Ratio)

Table 5. Color Documentation

cluster	pixels	name	HEX	RGB
a	29.42%	198,169,94 laser ΔE=2.6	#CAA860	202 168 96
b	26.95%	203,191,160 half pavlova ΔE=2.2	#CABB9C	202 187 156
c	23.63%	203,161,53 satin sheen gold ΔE=3.2	#CCA53E	204 165 62
d	20.00%	198,142,63 anzac ΔE=1.1	#C88F41	200 143 65

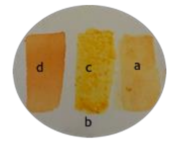


Figure 8. Resulted Color (a. 76v, b. standard 300 GSM watercolor paper, c. 104r, d. commercial)

As shown in **Table. 3**, Manuscript Based Historical Pigments (f.76v and f.104r) are classified as ASTM Lightfastness level I, while Commercial Historical Pigments are classified as level II. Therefore, Manuscript Based Historical Pigments show a better light fastness result than Market Historical Pigments.

Table 4. Light Fastness Test Result

	Delta E	ASTM Lightfastness
Commercial	6	II
f. 76v	2	I
f. 104r	3	I

Table 3. pH Test Result

	pH Value
Commercial	6.63
f. 76v	5.54
f. 104r	5.29

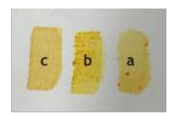


Figure 7. Pigments after 13hrs Xenon Arc Lamp(a. 76v, b. 104r, c. commercial)

However, as shown in **Table. 4**, Commercial Historical Pigments has a pH value closer to 7 than Manuscript Based Historical Pigments, showing it is less acidic, and demonstrates a milder character. The light fastness test and pH test show there are both strength and weakness in the Manuscript-Based Historical Pigments and Market Historical Pigments. This demonstrate the quality of Manuscript- Based Historical Pigments still need to further improve.

According to Opinion Based Description, different people have different opinion. For artists, the particle size of Manuscript Based Historical Pigments need to be smaller. However for conservators, the authentic color matters more.

Conclusion

In this project, we concluded that Manuscript-Based Historical Pigments and Market Historical Pigments each have their weakness and strength, and thus perform differently in the characterization test. In general, our project shows Manuscript-Based Historical Pigments prove to have more genuine color, expressed a need for Manuscript-Based Historical Pigments. However, the quality of Manuscript-Based Historical Pigments still need to improve. Future developments such as increasing water solubility and mass production should be considered.

Helen Zhang's reconstruction of The Lady in Gold (Gustav Klimt, 1907) using self-made pigment.