

Article

Novel Procedure for Brochantite Based Pigment Production and Its Immobilization for Restoration of Historical Copper Objects

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Abstract: The article deals with the preparation of artificial copper pigment based on brochantite. The pigment was prepared by slow additions of sodium hydroxide solution into the solution of copper sulphate. The studied parameters were addition rate, solutions concentrations, ferrous ion addition, and filtration time. The prepared pigments were evaluated by means of X-ray diffraction and spectrophotometry. Subsequent pigment immobilization in an acrylate varnish was also studied. Observed parameters were influenced by solvent type, mechanical or chemical dispersion, and natural aging in an aggressive outdoor atmosphere. Pigment containing varnishes were evaluated by means of spectrophotometry, optical profilometers, and pull-off test. Slow hydroxide addition allows the formation of brochantite pigment. Fast filtration limits backward pigment decomposition. Ferrous ion improves pigment color closer to natural copper patina. The ideal immobilization procedure includes ethylacetate as a solvent and mechanical dispersion. The varnish filled with pigment provides sufficient adhesion to the metallic copper substrate as well as long-term color stability in the outdoor atmosphere.

Keywords: brochantite; titration; artificial pigment; patina; filtration; immobilization

1. Introduction

Copper subjected to outdoor atmosphere is covered by natural patina, which is aesthetically acceptable [1–9]. Copper patina has been known since antiquity. The patina has dark brown-to-black color. When exposed to chloride or sulphur dioxide polluted atmosphere, the patina can turn a blue–green or green color, respectively. Since antiquity till nowadays people are trying to improve copper surface look by artificial patinas [10,11]. It is possible to detect four stages of natural patina. First, a cuprous oxide is formed, and the copper surface turns brown. Via metastable basic salt, the patina is transformed into final corrosion products based on sulphate (brochantite) or chloride (atacamite) [1,3,12]. The kinetics of patina formation are dependent on pollutant concentration in the atmosphere [6,13–18]. If the pollutant concentration is not sufficient, the patina based on oxides remains black [5,12,19–21]. Patina formed under inner terran industrial atmosphere of Central Europe is based solely on brochantite [22–24]. A procedure for brochantite pigment preparation was proposed, but without necessary parameters of the procedure [19,25]. Di Carlo G. et al. she tried to obtain patination from the aqueous solution with two chemicals CuCl_2 , CuSO_4 applied by cotton swabs with various concentration of this chemicals [26]. A patent from Gervais J. describes the process of artificial patination which involved the cleaning of any impurity from the surface of copper substrate, polishing the copper substrate with aqueous solution containing sodium ions, acetate ions, chlorine ions, sulphate ions, H^+ ions, and OH^- until a brown color is obtained [27]. In a patent from Hokazono

T. and Tanaka S. they try to obtain the artificial patination from aqueous phase which create the droplets on the copper surface. The procedure involves creation of uneven droplets of solution with copper sulfide and from this solution they can create the layer of artificial copper patination [28].

The aim of this work was to provide a procedure for production of brochantite pigment for local restoration of natural patina on copper objects. The procedure must be described in detail and must be robust and simple for pigment preparation in the restorers' workshop. The critical volume of the pigment in lacquer for our method was 1.5 g stirred into 25 mL 10% solution of Paraloid B48N. This volume of the pigment was a best for the application on the copper surface. We tried to increase the dispergation of the pigment and for this we used the commercial dispersant Tego 655, 674, 675, 685, 689, and 690 which we added 1 mL respectively 1 g from each.

2. Experimental

2.1. Small Volume Experiments

The experiments were carried out using automatic titration device HI 901 (*Hanna Instruments*). Solutions of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were titrated by solutions of sodium hydroxide (NaOH). Concentration of titrant was $0.1 \text{ mol} \cdot \text{dm}^{-3}$ for copper sulphate solution of concentration $0.01 \text{ mol} \cdot \text{dm}^{-3}$ or $1 \text{ mol} \cdot \text{dm}^{-3}$ for copper sulphate solutions of concentration 0.1, 0.4 and $0.626 \text{ mol} \cdot \text{dm}^{-3}$ saturated (solution). Volume of the titrated copper sulphate solution was 100 mL, and it was intensively stirred in 250 mL beaker by 20 mm magnetic stirrer ($250 \text{ rot} \cdot \text{min}^{-1}$). The rates of titrant additions were 0.8, 0.5, 0.04, and $0.01 \text{ mL} \cdot \text{min}^{-1}$. Additions of 0.007 and $0.001 \text{ mol} \cdot \text{dm}^{-3}$ ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) into $0.04 \text{ mol} \cdot \text{dm}^{-3}$ copper sulphate solution were tested. When pH reached 11 the solution was filtered using Buchner funnel with standard laboratory glassy vacuum ejector. Filtered pigment particles were immediately washed twice with 100 mL of demineralised water. The pigment was consequently dried in the oven at $60 \text{ }^\circ\text{C}$.

2.2. Large Volume Experiments

Previous experiments allowed the preparation of pigment in the order of units of grams. Therefore, a large volume titration was studied. The volume of $0.626 \text{ mol} \cdot \text{dm}^{-3}$ copper sulphate solution was 5 dm^3 in the cylindrical polyvinylchloride bucket of 0.3 m diameter and 0.3 m height. Titrant had concentration $1 \text{ mol} \cdot \text{dm}^{-3}$. Dosing rate was 1, 2, 5, and $10 \text{ mL} \cdot \text{min}^{-1}$. Stirring was done by ER10 (*MLW*) rotating $2700 \text{ rot} \cdot \text{min}^{-1}$ glassy rod stirrer with 2 rectangular ($50 \text{ mm} \times 20 \text{ mm}$) blades. Solution was filtered on special filtering device (self-produced) with filtering textile and rotating pump, allowing filtering of $22 \text{ dm}^3 \cdot \text{min}^{-1}$ of liquid. Prepared pigments were dried in the oven at $60 \text{ }^\circ\text{C}$ and milled in the ball mill 5.250SP1-VM (*LabTest*, Prague, Czech Republic).

Phase composition of prepared pigment was analysed by XRD device X'Pert Pro (*PANalytical*, Prague, Czech Republic) and color was evaluated by spectrophotometer CM-700d (*Minolta*, Prague, Czech Republic).

2.3. Pigment Immobilization

The pigments were immobilized on the $50 \text{ mm} \times 50 \text{ mm}$ copper sheet by 10% solution of acrylate varnish Paraloid B48N (copolymer of butylacrylate and methylmethacrylate). Xylene, acetone, and ethylacetate were used as solvents. The amount of added pigment was 25 g per 100 mL of varnish solution. Mechanical dispersion of pigment aggregates in the varnish solution was carried out using a standard kitchen blender. Chemical dispersion was done using commercial surface-active compounds. Therefore, they are assigned only with number codes without chemical specifications.

Besides spectrophotometry, the prepared samples were tested using optical profilometer SJ-201 (*Mitutoyo*, Prague, Czech Republic) and pull-off testing device Comtest OP (*Coming Plus*, Prague, Czech Republic). Cross cuts of the samples were observed by means of scanning electron microscope VEGA3 LMU (*TESCAN*, Prague, Czech Republic).

Sets of four samples prepared using each solvent were exposed for one year on the outdoor exposure station in Ostrava-Radvanice (Czech Republic) with increased content of sulphur dioxide (in peaks exceeding $100 \mu\text{g}\cdot\text{m}^{-3}$).

3. Results and Discussion

3.1. Small Volume Experiments

The set of dynamic titrations of $0.01 \text{ mol}\cdot\text{dm}^{-3}$ copper sulphate solution by $0.1 \text{ mol}\cdot\text{dm}^{-3}$ sodium hydroxide solution was carried out first to estimate inflection point and final pH. The example of the curve is given in Figure 1. The final value of pH for the preparation procedure was estimated at pH 11. Dynamic titration provided completely blue pigment based on cupric hydroxide ($\text{Cu}(\text{OH})_2$).

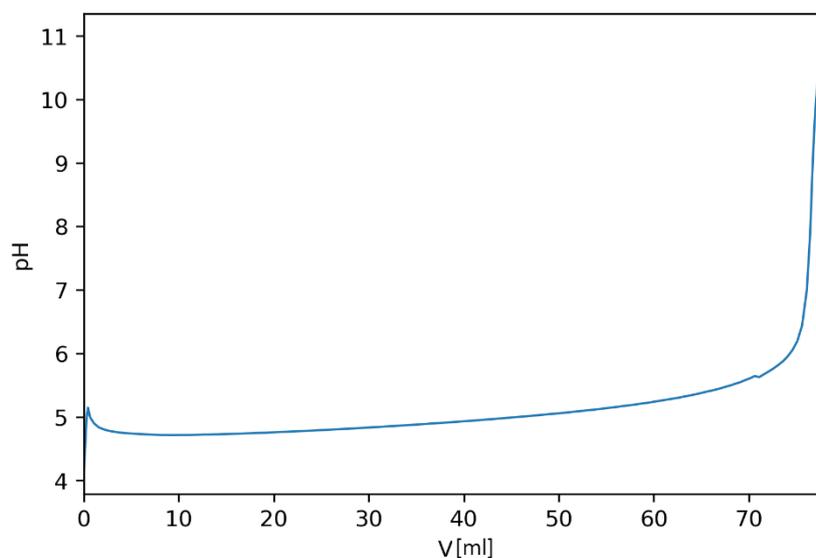


Figure 1. Dynamic titration of 100 mL of $0.01 \text{ mol}\cdot\text{dm}^{-3}$ solution of CuSO_4 by $0.1 \text{ mol}\cdot\text{dm}^{-3}$ solution of NaOH .

It was obvious that the alkali dosing rate must be decreased. The dosing rate $0.8 \text{ mL}\cdot\text{min}^{-1}$ still provided major amount of cupric hydroxide and minor portion of cupric oxide—tenorite (CuO). The addition rate $0.5 \text{ mL}\cdot\text{min}^{-1}$ showed the first marks of basic sulphate presence. The major portion was formed metastable posnjakite ($\text{Cu}_4(\text{OH})_6\text{SO}_4\cdot\text{H}_2\text{O}$) which is a precursor for brochantite ($\text{Cu}_4(\text{OH})_6\text{SO}_4$). The XRD results are summarized in Figure 2. A decrease of dosing rate to $0.04 \text{ mL}\cdot\text{min}^{-1}$ allows formation of significant portion of brochantite, while further deceleration of dosing rate to $0.01 \text{ mL}\cdot\text{min}^{-1}$ led to nearly complete transformation of posnjakite to brochantite. The color of this completely brochantite based pigment is shown in Figure 3a. It is still slightly bluish. This is confirmed by spectrophotometry in the same figure. The 'a' and 'b' coordinates of CIELab color space are shown. The color of pigment is shifted in a blue direction from natural patina (from the roof of Queen's Anne Summer Palace in Prague). Additions of ferrous ions into the $0.04 \text{ mol}\cdot\text{dm}^{-3}$ copper sulphate solution allowed to shift the color in yellow direction. The addition of $0.007 \text{ mol}\cdot\text{dm}^{-3}$ ferrous ions changed the color beyond the acceptable limit Figure 3b. The addition of $0.001 \text{ mol}\cdot\text{dm}^{-3}$ ferrous ion improved the color into the almost identical one to the natural patina Figure 3c. In addition, ferrous ions probably acted as nucleation agents and they allowed formation of exclusive brochantite pigment even at higher dosing rate $0.04 \text{ mL}\cdot\text{min}^{-1}$.

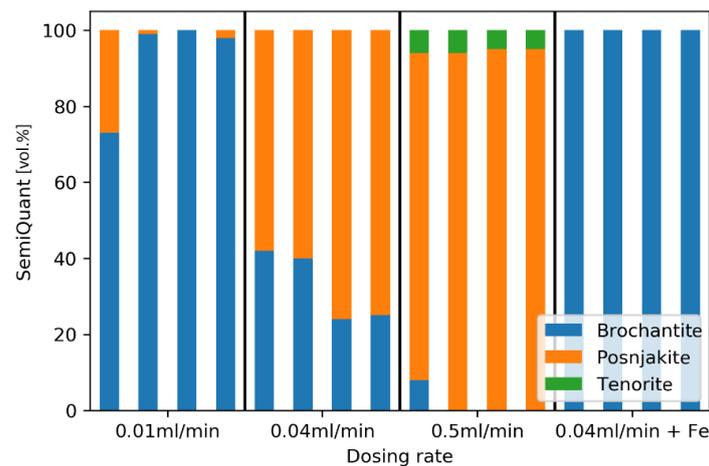


Figure 2. Influence of dosing rate of $1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH into $0.626 \text{ mol}\cdot\text{dm}^{-3}$ CuSO_4 and ferrous ions addition ($0.001 \text{ mol}\cdot\text{dm}^{-3}$) on phase composition of produced pigment estimated by means of XRD.

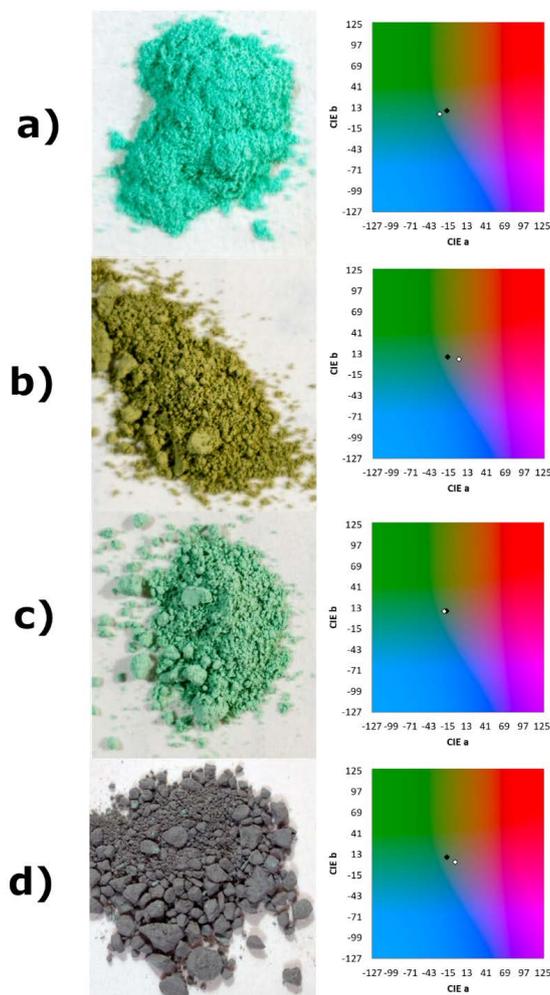


Figure 3. Spectrophotometry results displayed in CIE Lab coordinates [29] and their comparison to natural patina prepared by $0.04 \text{ mL}\cdot\text{min}^{-1}$ dosing rate of $1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH into 100 mL of $0.626 \text{ mol}\cdot\text{dm}^{-3}$ CuSO_4 (a); with ferrous ions addition $0.007 \text{ mol}\cdot\text{dm}^{-3}$ (b); ferrous ions addition $0.001 \text{ mol}\cdot\text{dm}^{-3}$ (c); and $10 \text{ mL}\cdot\text{min}^{-1}$ dosing rate of $1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH into 5 L of $0.626 \text{ mol}\cdot\text{dm}^{-3}$ CuSO_4 with ferrous ions addition $0.001 \text{ mol}\cdot\text{dm}^{-3}$ and slow filtering procedure (d).

1 L·min⁻¹ (Figure 2). The mixing speed of the solution did not significantly affect the grain size of the patina formed. The only difference was in the volume of patina created. With increasing concentration of CuSO₄ solution, the volume of patina produced also increased, whereas if we increased the concentration of NaOH, the end point was reached faster, but almost no patina grains precipitated. The dosing rate of NaOH affected the final patina grain yield. The higher the dosing rate of NaOH, the lower yield. The probable cause of this was insufficient reaction of the CuSO₄ solution with the NaOH solution. We chose 0.04 mL/min for the optimal addition rate.

3.2. Large Volume Experiments

Large volume experiments started with magnetic stirrer, which was not powerful enough. It allowed local over-alkalization and precipitation of cupric hydroxide. Therefore, it was replaced with a more powerful glassy rod stirrer. This intensive stirring allowed to use dosing rate 10 mL·min⁻¹ of 1 mol·dm⁻³ sodium hydroxide into 5 dm³ of 0.626 mol·dm⁻³ copper sulphate solution (with 0.001 mol·dm⁻³ ferrous sulphate). This dosing rate is 5 times higher compared to the small volume experiments. The stirring is evidently one of the key parameters and more intense stirring allows increase of dosing rate without danger of local over-alkalization.

During the filtering another key parameter was observed time to complete the filtering and washing. Solutions were first filtered by means of 2 dm³ Buchner funnel. This procedure took approximately 2 h. It was too slow and exposure in alkalkine solution led to decomposition of brochantite to tenorite. Tenorite is present as thick layer on the surface of the pigment particles and it shifts their color to grey (Figure 3d). On the contrary, if hydroxide solution addition was done to reduce the pH below 11, the precipitation efficiency decreased from 42%–48% to values below 20%.

The utilization of special filtering device (Figure 4a) allowed faster filtering decreasing the time to complete filtering and washing to 3 min. The prepared pigment had a similar color (Figure 4b) as the small volume ideal pigment (Figure 3c). In total, five campaigns were done with the ideal procedure. Their color evaluation is given in Figure 5. Large volume precipitation is evidently very sensitive to any negligible change of local solution composition and even under the same procedure, we can obtain significant deviation in color. Nevertheless, after milling and homogenizing we can obtain pigment with color close to the natural patina.

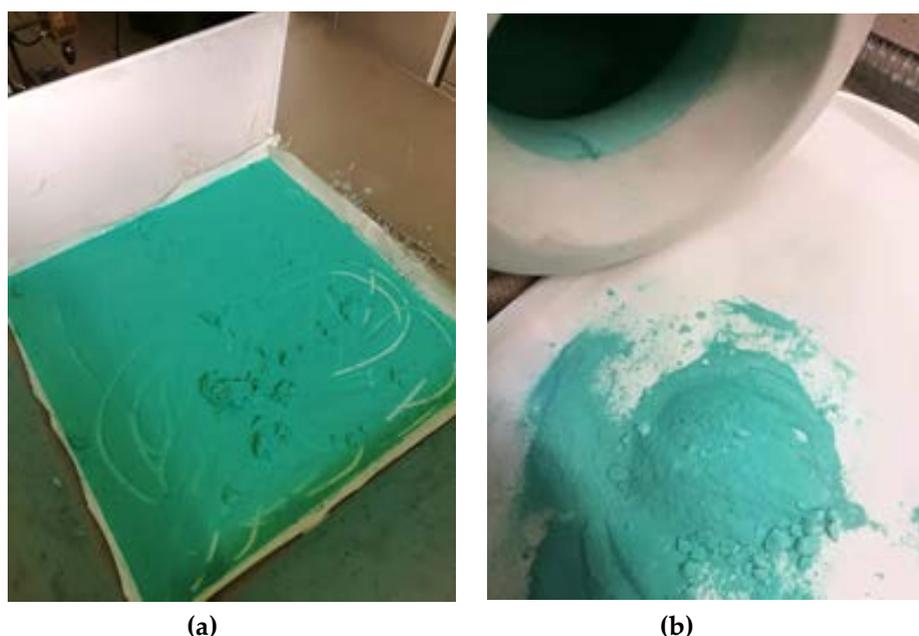


Figure 4. (a) Special filtering device allowing fast filtering procedure and (b) pigment produced after ball milling.

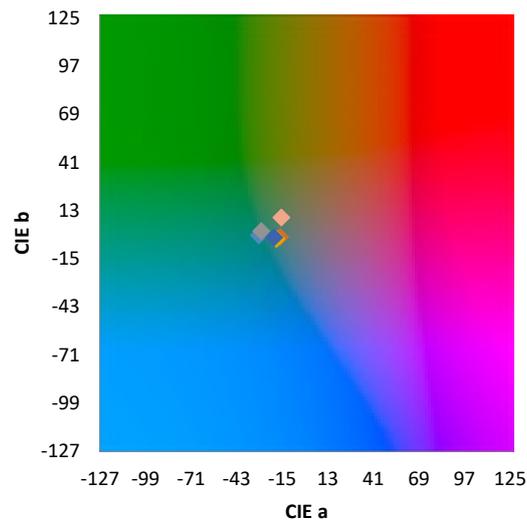


Figure 5. Color (CIELab) of five independent production campaigns.

3.3. Pigment Immobilization

Basic varnishes containing the pigment without dispersion were studied by SEM on cross sections. An example of the xylene solved varnish layer is given in Figure 6. Using a backscattered electron detector, it is obvious that the pigment formed aggregates up to a diameter corresponding to the layer thickness. The ability to form aggregates is well described by much simpler and faster method—optical profilometry. Surface roughness is a measure of pigment aggregation. Without mechanical dispersion, the ability to form aggregates is influenced by solvent polarity and its wettability to the pigment particles. The most polar solvent, ethylacetate, shows the best wettability and the lowest surface roughness (Figure 7). Xylene had the highest roughness due to its low polarity. However, after mechanical dispersion high viscosity of the varnish solution in xylene has a significant effect, which did not allow reverse aggregation of dispersed pigment particles. When chemical surfactants were used to improve the wettability of the pigment particles in varnish solution, they affected the color of the pigmented varnish mostly to bluish (see example of 675 chemical dispersion containing varnish in Figure 8). The only dispersant, which did not change the color, was type 655. On the contrary, the dispersant 655 did not improve the wettability (roughness) as significantly as 675, see Figure 9.

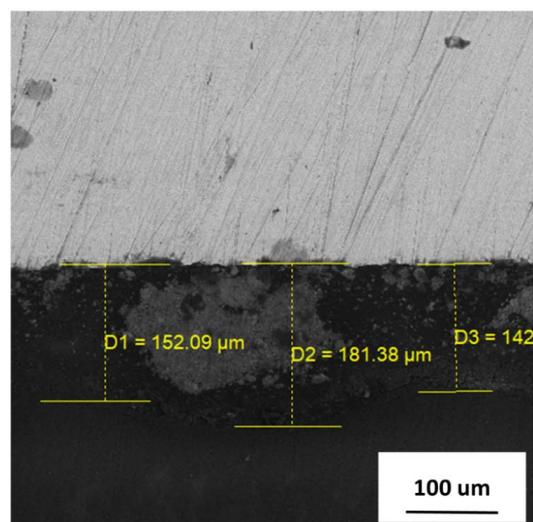


Figure 6. BSE image of pigment immobilized in Paraloid B48N varnish solved in xylene.

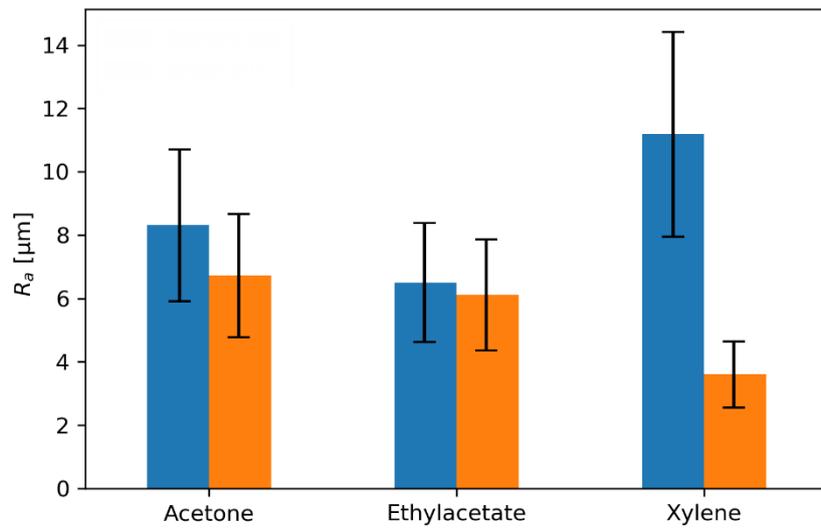


Figure 7. Surface roughness of pigment containing varnish coatings solved in different solvents without dispergation (blue) and with mechanical dispergation (orange).

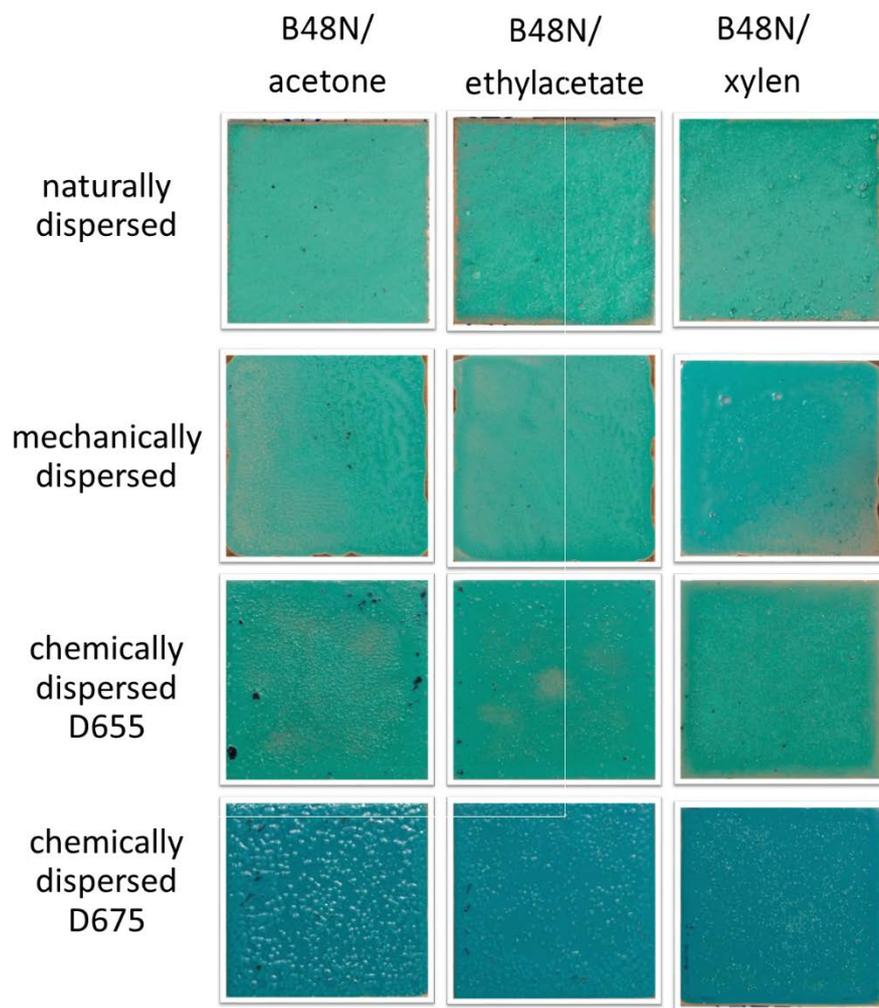


Figure 8. Effect of dispergation type on color of different varnish systems.

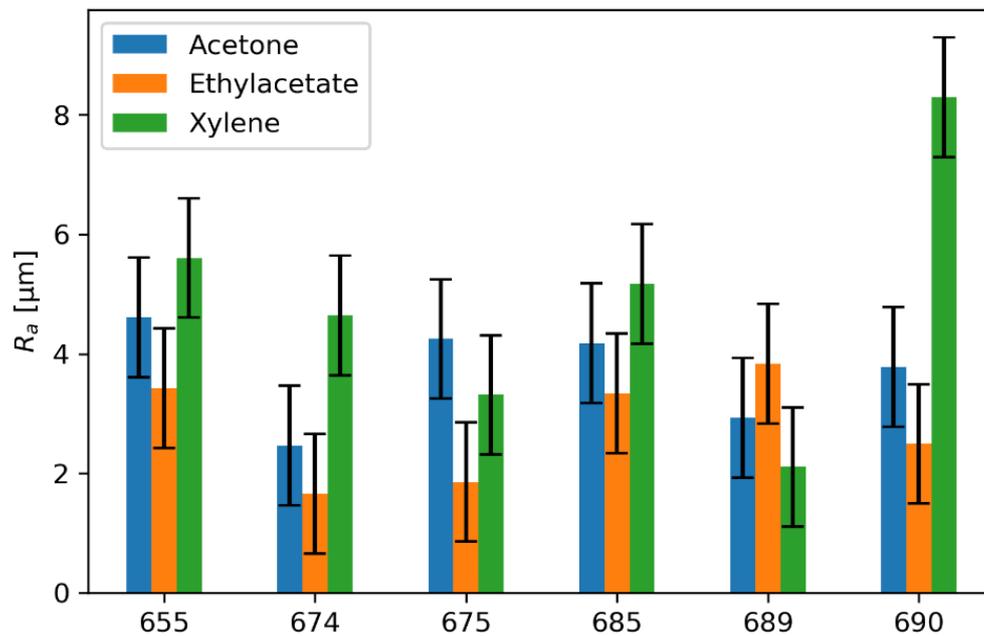


Figure 9. Effect of different chemical dispersant on surface roughness of varnish systems.

The samples coated with pigmented varnish were evaluated also after one-year exposure in the outdoor atmosphere. The color changed significantly on some of the samples, while marginally on the others (Figure 10). These color changes were caused by dust particles incorporated in the surface and not by any change of pigment color or varnish properties. The absence of change in varnish properties was also confirmed also by pull-off adhesion tests (Figure 11). The adhesion to copper substrate rather increased after the exposure. It was probably caused by natural curing of the varnish due to evaporation of residual solvent and better polymer cross-linking. The highest adhesion was observed on samples prepared with ethylacetate as solvent.

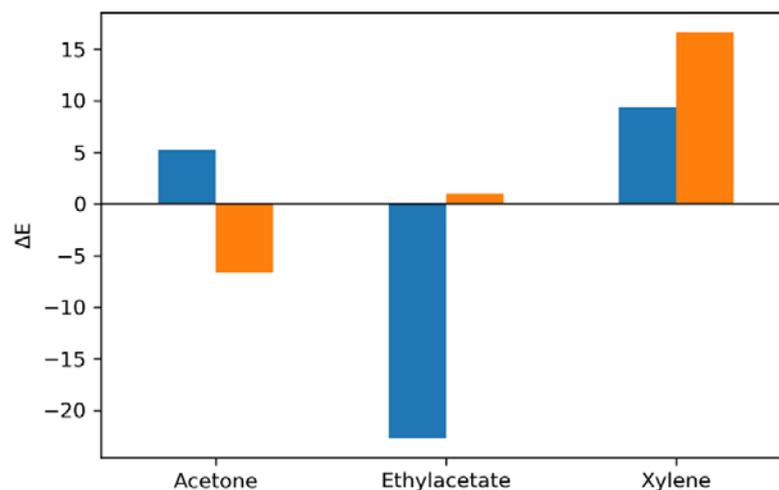


Figure 10. Change of color after one-year outdoor exposure (two samples of each varnish system); direct comparison to color before exposure.

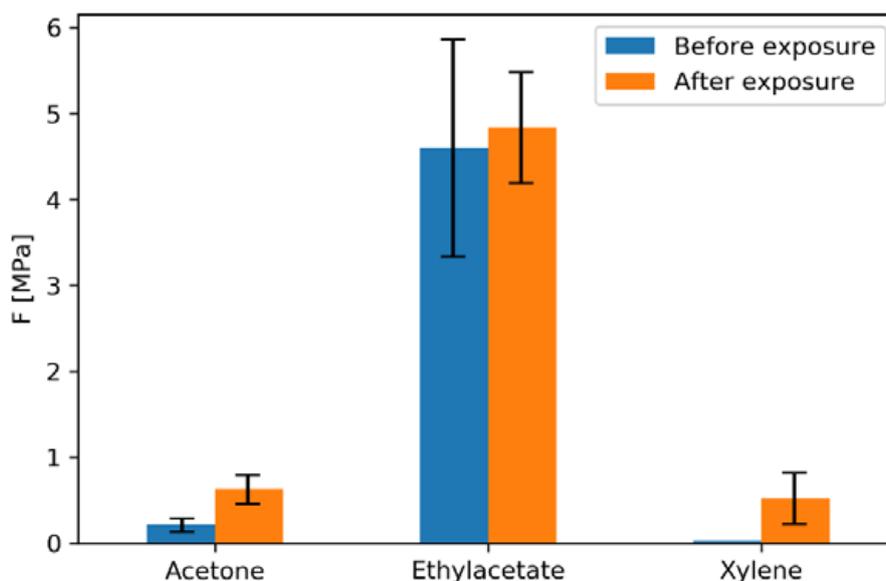


Figure 11. Adhesion of varnish systems estimated by pull-off test.

4. Conclusions

The key parameters of pigment production are concentration of sodium hydroxide and copper sulphate solutions, dosing rate, and stirring intensity. The higher the concentration and dosing rate are, the more intensive stirring is necessary to avoid local over-alkalization. The addition of ferrous ions improves the color of brochantite pigment closer to natural patina. Another key parameter valid especially during large volume productions is fast filtration of the solution after pigment precipitation. It is necessary to filter and wash the pigment twice within 3 min after reaching pH 11.

Ethylacetate accompanied by mechanical dispersion is the optimal procedure of immobilization of pigment into acrylate varnish. It provides homogeneous color and high adhesion to the substrate. Outdoor exposure does not change its good properties. In the article from Fitzgerald et al. [19] a method of creating a copper patina directly from solution is used. In contrast, our method works with the precipitation of pigment from a solution, which is then mixed in a lacquer and applied to a copper surface. Our method differs from that of the Fitzgerald et al. article in that we use titration and rapid mixing to form the pigment and then immobilize it on the lacquer. At the same time, this lacquer layer also serves as additional patina protection in some cases. There are still a few patents from authors such as Atrons [25] and Gervais [27] who use either patination directly from solution or using pastes that form a patina. The benefit of our method is that we are able to create a very accurate copy of the natural patina and at the same time we do not have to additionally protect the patina layer, because using the right varnishes will create a protective layer that protects the patina as a side effect.

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Conflicts of Interest: The authors declare no conflict of interest.

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