

THE STABILITY OF CADMIUM CHALCOGENIDE PIGMENTS IN THE PROCESS OF LASER CLEANING OF PAINTED SURFACES*

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Pigments based on cadmium selenide sulphides and cadmium sulfides were analysed as regarding their structure and stability against the laser irradiation, a new technique for cleaning the painted surfaces in artwork restoration. The pulsed Nd:YAG laser radiation determines the effusion of some sulphur from the red pigment Cd(S,Se) and significant decrease of the average size of the crystallites. The color turns to dark red. For yellow pigment (CdS) no change of crystallite size was detected after laser irradiation.

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1. Introduction

The application of laser in artwork restoration and conservation is a challenging problem for specialists due to the necessity to find the exact regime of irradiation, which does not affect both physically and aesthetically the painted surfaces.

The cadmium red and cadmium yellow are considered relatively new colours and they are largely used since the beginning of the 80th century by the greatest [1] painters: De Stael, P. Picasso, H. Matisse. The cadmium pigments are used, also, as colouring agents in enamelling, glass-making and ceramic industries [2] as well as for printing inks and varnishes.

The development of the colour in the yellow glasses with CdS is due to the production of a colloidal precipitate of cadmium sulphide. If increasing amounts of selenium are added to a glass containing CdS, the yellow colour is replaced first by an orange colour and finally by a brilliant red colour known as the selenium ruby. The colouring agents in such glasses appear to be crystals of colloidal dimensions. These crystals can be described as cadmium sulpho-selenides representing members of a series of mixed crystals between cadmium sulphide (CdS) and cadmium selenide (CdSe).

In this paper we discuss the results of a study related to the structure of the cadmium red and Cd yellow pigments and the influence of the YAG: Nd laser radiation on their properties.

2. Experimental

Powders of cadmium red and cadmium yellow pigments were purchased from MAIMERI S.p.A, product PR 108 – Cadmium Red Medium and product PY 35 – Cadmium Yellow Light.

X-ray diffraction analysis were carried out by diffractometric method. A TUR M-62 diffractometer provided with copper target tube. X-ray diffracted quanta were collected at equal θ steps of 0.01° within a time interval of 10s for every angular step. The diffraction data were processed using the resources of a PC.

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A YAG:Nd laser emitting on the wavelength of 1064 nm in pulsed regime was used in the irradiation experiments. Fluences of 20 and 40 mJ/cm² and two shots for every point of the sample surface was the standard irradiation.

Transmission Electron Microscopy (TEM) was performed on fresh, not irradiated powders.

3. Results

3.1. X-ray diffraction

The X-ray diffraction diagrams of cadmium red and cadmium yellow powders are shown in Figs. 1 and 2. Only crystalline phases are evidenced on the diagrams.

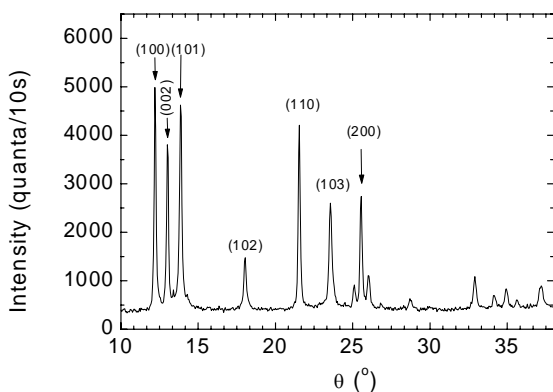


Fig. 1 The X-ray diffraction diagram of cadmium-red powders.

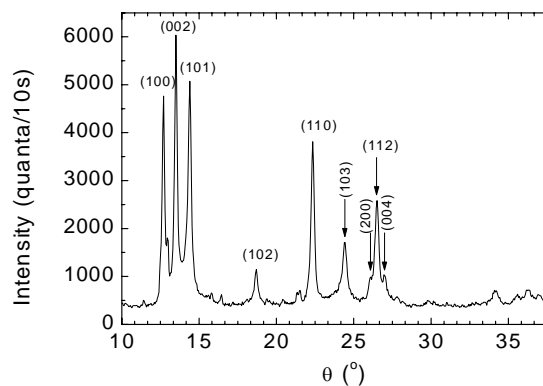


Fig. 2 The X-ray diffraction diagram of cadmium-yellow powders.

The crystallographic phases were identified with the X-ray powder diffraction files (XPDF) [3]. The cadmium red powder is a Cd(S,Se) phase. Careful measurements of the positions of the X-ray diffraction lines allow to identify a hexagonal phase with a composition near Cd₁₀S_{5.7}Se_{4.3} or 43 mole % CdSe in the CdS-CdSe solid solution.

The profile of the X-ray diffraction peak (103) situated at $\theta = 23.6^\circ$ was measured with high accuracy with the aim to calculate, from the line width, the mean size of the crystallites in the powder. As reference sample has been used a gold film deposited on glass substrate. A value of 142 nm was obtained for mean size of the crystallites in cadmium-red pigments before irradiation and 86 nm after irradiation with high fluence radiation (40 mJ/cm²).

Careful measurements of the positions of the diffraction peaks of cadmium red powder, before and after laser irradiation have shown a slight shift towards low diffraction angles (e.g. – 0.06° (2 θ) in the case (103) peak) for irradiated samples. This fact speaks in favour of an increase of the lattice constants of the hexagonal phase.

It is known from the crystallography of the CdS-CdSe solid solution that by decreasing the sulphur content, the hexagonal lattice expands. We can conclude that laser irradiation determines the elimination of sulfur. Such effect of effusion in sulphur containing chalcogenides has been already reported [4] after irradiation by high energy UV radiation.

In the case of cadmium yellow pigment (Fig. 2) the crystallographic phase shows hexagonal symmetry and was identified as the CdS phase ($a=0.4136$ nm, $c=0.6713$ nm). The accurate recording of the profile of the peak (103) allowed for the calculation of the mean size of the crystallites: 37 nm. No change of peak width and position was revealed after irradiation of the sample surface in the same conditions as for cadmium red pigment sample.

3.2 Transmission electron microscopy

More information regarding the structure and morphology of the powders has been obtained by TEM studies.

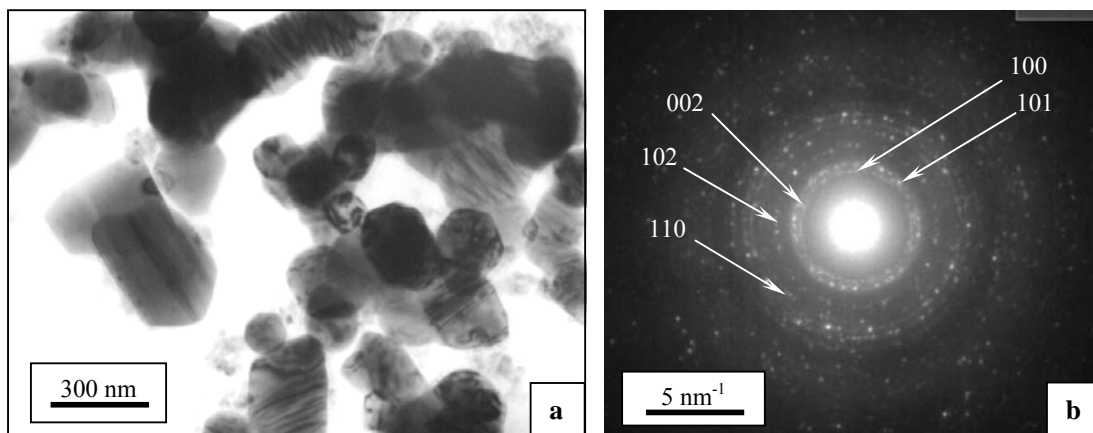


Fig. 3 (a) Agglomeration of cadmium-red crystallites with an average grain size around 200 nm; (b) the corresponding diffraction pattern revealing a hexagonal structure; the main diffraction rings are indicated by arrows.

A typical agglomeration of cadmium-red crystallites is presented in Fig. 3a, where the average grain size is around 200 nm. The corresponding diffraction pattern (Fig. 3b) confirms the XRD results revealing a hexagonal crystalline phase slightly different from pure CdSe. This particular structure ($a = 0.418$ nm, $c = 0.788$ nm) is distorted compared to the pure CdSe hexagonal structure ($a = 0.429$ nm, $c = 0.701$ nm), due to the presence of S atoms in the lattice, as revealed by XRD analysis. Crystal grains contain a high density of stacking faults along the c axis as shown in Fig. 4a, leading to the appearance of diffuse streaks between the diffraction spots (Fig. 4b) parallel to the reciprocal vector g_{002} .

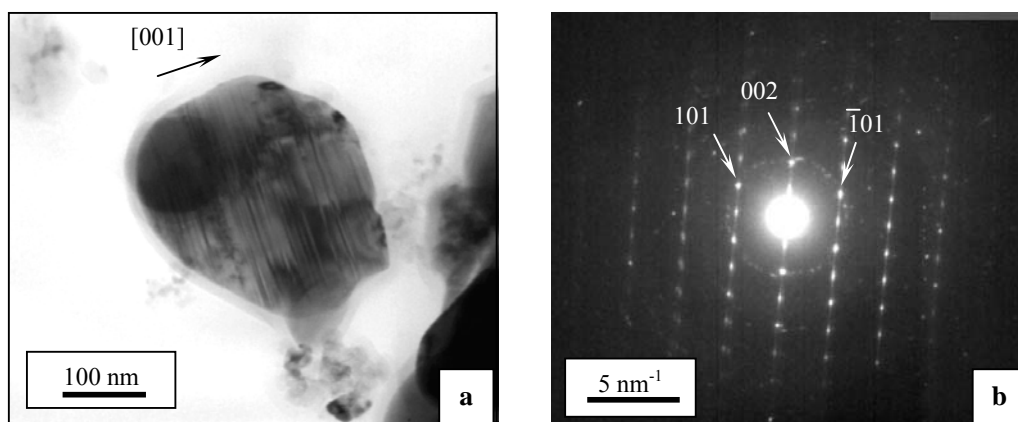


Fig. 4. (a) Crystal grain showing a high density of stacking faults along the c axis; (b) diffraction pattern along the $\vec{B} = [010]$ zone axis; diffuse streaks between the diffraction spots indicate a high density of stacking faults.

A low magnification TEM image of the cadmium-yellow sample (Fig. 5a) shows a powder with a finer granularity than the cadmium-red powder. The corresponding diffraction pattern evidences the hexagonal structure of the CdS.

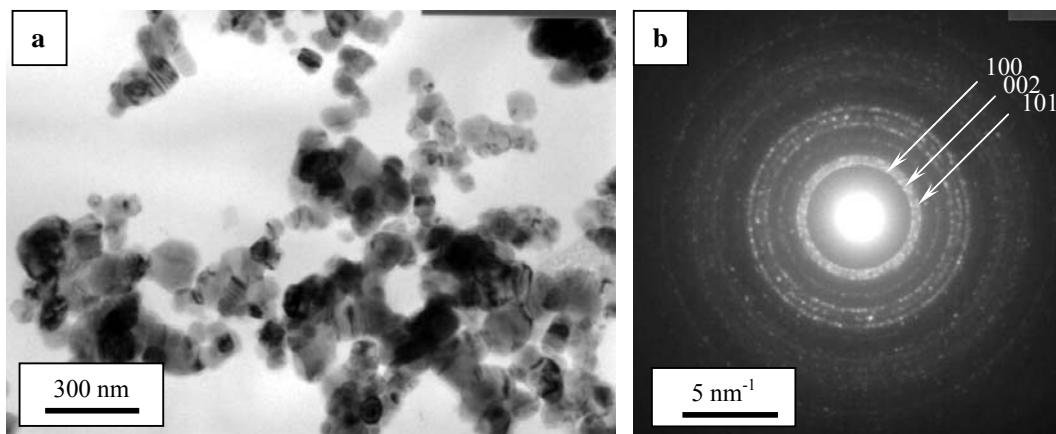


Fig. 5. (a) Wide-field view of the cadmium-yellow powder; (b) the corresponding SAED pattern; a few main diffraction rings are indicated by arrows.

Larger sized grains are relatively rare and show a high density of planar faults as shown for example in Fig. 6a. The 100 spots in the corresponding diffraction pattern taken along the [001] crystallographic direction (Fig. 6b) are elongated according to the direction of the stacking faults visible in Fig. 6a.

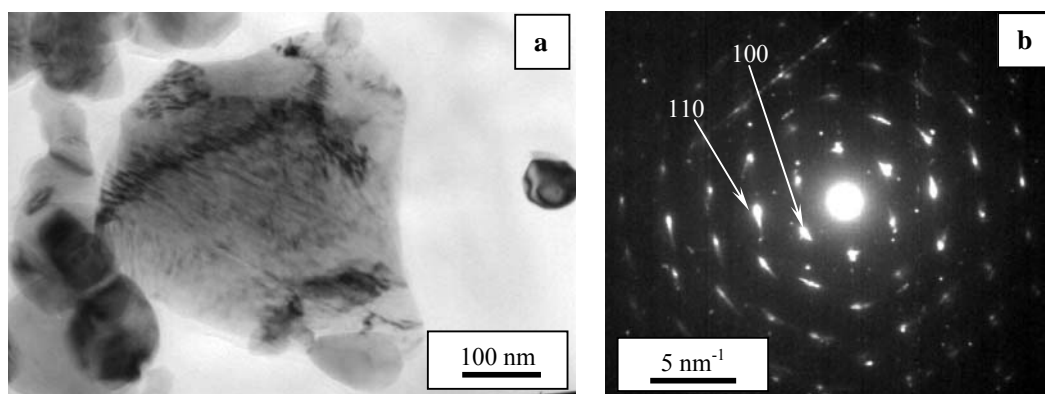


Fig. 6. (a) Large crystal grain showing a high density of planar faults; (b) the corresponding SAED diffraction pattern along the c axis showing elongated spots due to the presence of a high density of planar faults.

3.3 Fluence effect in laser cleaning

Important and direct methods of investigation of the colour alteration after a controlled laser treatment is colorimetric analysis and even naked-eye inspection – agreed by all schools of restoration.

Two samples of Cd red tempera – prepared with egg emulsion - and two samples of Cd red oil color – prepared with linseed oil – were measured before irradiation and after Nd:YAG laser irradiation with two distinct working regimes.

A computer driven spectrophotometer with diffuse illumination, and with 8° viewing was used at scanning steps 1-20 nm. Wavelength range of analysis was between 400 and 700 nm.

Reflectance values for each preparation are presented on the same diagram for a comparative interpretation.

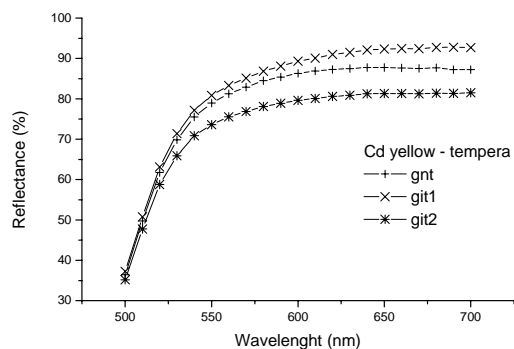


Fig. 7. Reflectance curves for Cd Yellow tempera.

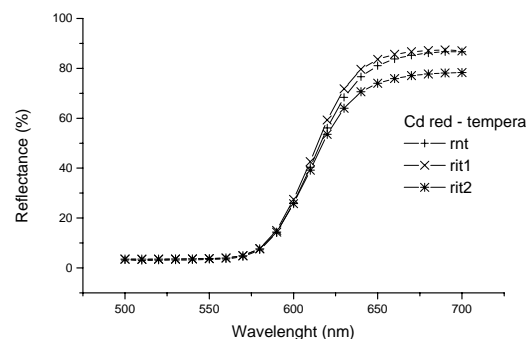


Fig. 8. Reflectance curves for Cd Red tempera.

Fig. 7 shows the reflectance of the Cd yellow sample before irradiation [gnt], after irradiation with low fluence (20 mJ/cm^2) represented by {git1} and after irradiation with high laser fluence (40 mJ/cm^2) represented by {git2}. Fig. 8 shows other three diagrams that correspond to similar measurements on Cd red sample. Significance of the lines are the following: {rnt} – reflectance before irradiation, {rit1} – reflectance after irradiation with low laser fluence (20 mJ/cm^2), and {rit2} – reflectance after irradiation with high laser fluence (40 mJ/cm^2).

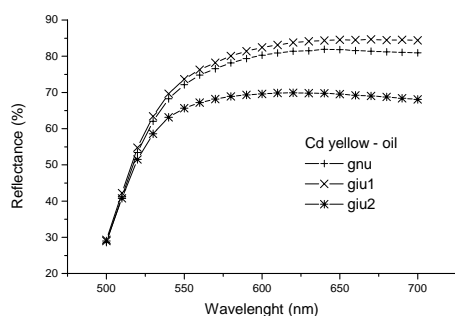


Fig. 9. Reflectance curves for Cd Yellow oil.

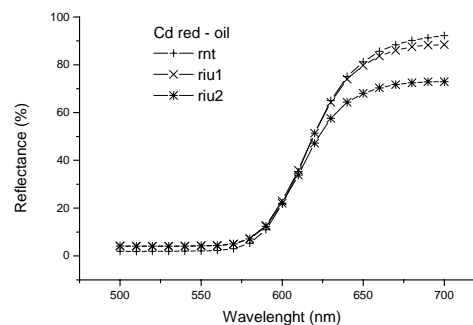


Fig. 10. Reflectance curves for Cd Red oil.

Figs. 9 and 10 present the reflectance values for Cd yellow oil colour and Cd red oil colour picked-up in similar experimental conditions.

It results that low energy regime of irradiation does not affect significantly the colour of the Cd chalcogenides.

4. Discussion

The red and yellow colour of the cadmium chalcogenides are strongly related to the ratio sulphur/selenium in the hexagonal $\text{Cd}(\text{S},\text{Se})$ compound. The mixed compound with sulphur and selenium approaching the fifty-fifty composition is influenced by laser radiation. Some sulphur is eliminated, the hexagonal lattice expands and the colour turns to dark red. The modification of the colours seems to be related both to the elimination of sulphur and to decrease of the average size of the $\text{Cd}(\text{S},\text{Se})$ crystallites. In the case of the yellow Cd pigments the CdS crystallites are stable against laser radiation. Nevertheless, a change of colour toward dark yellow speaks in favour of a process of elimination of sulphur during laser irradiation.

Scanning electron microscopy confirms the above X-ray diffraction results related to crystallite modifications, when laser beam is acting. The cleaning process was tested for two fluences: 20 and 40 mJ/cm^2 . The efficiency of the cleaning depends on the fluences.

In order to preserve the authentic colour of painture and to avoid the red and yellow colour to turn to dark ones, the high laser fluence must be avoided.

5. Conclusions

The cadmium chalcogenides pigments are constituted of Cd(S,Se) for the red pigment and CdS for the yellow one. The mean size of crystallites are 142 nm for cadmium red pigment and 37 nm for cadmium yellow pigment. As a result of laser irradiation the crystallite mean size of the red pigment decreases and the lattice expands due to sulphur elimination. The cadmium yellow pigment is structurally stable and exhibits crystallites with average size of 37 nm. During laser cleaning process, it should be applied to painture a soft irradiation regime, to avoid the original colour to turn dark.

References

- [1] S. Zuffi, Francesca Castria, Modern Painting, Electa, Milano, 1998.
- [2] P. W. McMillan, Glass-Ceramics, Academic Press 1964, p.73.
- [3] ASTM, XPDF, Fiche No. 40-837, 40-838; 6-0314.
- [4] M. Popescu, F. Sava, A. Lőrinczi, E. Skordeva, P.-J. Koch, H. Bradaczek, J. Non-Cryst. Solids, **227-230**, 719 (1998).
- [5] M. Castillejo, M. Martin, D. Silva, T. Stratandaki, D. Anglos, L. Burgio, R. J. H. Clark "Analysis of pigments in polychromes by use of laser induced break down spectroscopy and Raman microscopy", J. Mol. Struct. **550-551**, 191-198 (2000).
- [6] R. Radvan, N. Popescu, S. Dan, C. Comsia, "Chromatic Analysis of the Pigments Behavior after Laser Irradiation", ROMOPTO'2000, Vol. SPIE (in print).