LIGHT-SURFACE INTERACTION IN THE STUDY OF THE RESTORED PAINTINGS*

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This paper deals about a new method to restoration old paintings, based on light-surface interaction. Diffuse reflectance spectra can offer information on the electronic absorption spectra of the pigment samples, to be used to reduce the metamerism phenomenon. By mixing modern blue pigments with titanium white it is possible to obtain pigments azurite imitative retouching.

Key words: Painting, restoration, metamerism, electron microscopy, diffuse reflectance spectroscopy.

1. INTRODUCTION

In the practices of painting restoration the ancient pigments must be substituted by mixtures of synthetic pigments and colorants with similar diffusive reflectance spectra [1].

The surface color strongly depends on the spectral composition of the light used for illumination. Two identical surfaces have identical colors if they are painted with the same pigments and are illuminated with light of the same spectral composition. Colors which match in one set of viewing conditions but are not in ones are called metameric and this phenomenon is named metamerism [2].

Traditional icons are usually painted in egg tempera (Figure 1). In order to be restored they need to be cleaned with alcoholic gels [3].

Azurite, Cu₃(CO₃)₂(OH)₂, is the blue pigment often encountered on Byzantine icons. The present investigation was made to clarify which of the blue modern pigments have almost the same light-surface interaction as azurite [4].


2. EXPERIMENTAL

The structure and composition of the painted surfaces were investigated by electron microscopy (TESLA BS 300).

The light – surface interaction of different pigment mixtures is monitored by diffuse reflectance spectroscopy, DRS, on a SPU2P spectrophotometer using a Kubelka – Munk processing. The measurements were made in the visible range.

Samples of ancient azurite and modern pigments (manganese blue, Monastral blue, cerulean blue, cobalt blue and Prussian blue) were mixed in 5% of leaf gelatin in water and painted out into acid free cards.

Samples of blue pigments mixtures, $10^{-3}$–$10^{-1}$ M pigment in standard white ($\text{TiO}_2$), were mixed in 5% of leaf gelatin in water and painted out into acid free cards.

4. RESULTS AND DISCUSSIONS

Some cross sections were analyzed using an electron microscope TESLA BS 300. This allowed stratigraphic information to be collected (Figure 2).
The cross section of icon of the part of iconostasis from the church of Sts. Emperors Constantine and Helena in Iasi (19th Century) is typical for the neoclassical style [4,5].

Diffusive reflectance spectra (DRS) offer information about the electronic absorption spectra of the sample. The color of inorganic pigments arise from ligand field, charge transfer or intervalence charge transfer transitions, specular reflectance (Table 1) [6].

Table 1
Absorption bands and transition for studied pigment

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Chemical name</th>
<th>Formula</th>
<th>Absorption bands nm</th>
<th>Transition*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azurite</td>
<td>Basic copper (II) carbonate</td>
<td>Cu₃(CO₃)₂(OH)₂</td>
<td>740</td>
<td>LF</td>
</tr>
<tr>
<td>Azurite/Titanium white</td>
<td></td>
<td></td>
<td>520 620 740</td>
<td>CT,LF</td>
</tr>
<tr>
<td>Cerulean Blue</td>
<td>Cobalt (II) stanate</td>
<td>CoOₓSnO₃</td>
<td>450 587 700</td>
<td>LF</td>
</tr>
<tr>
<td>Cobalt Blue</td>
<td>Cobalt (II) aluminate</td>
<td>CoAl₂O₄</td>
<td>450 600</td>
<td>LF</td>
</tr>
<tr>
<td>Ultramarine</td>
<td>A complex sulfur-containing sodium aluminum silicate</td>
<td>Na₈₋₁₀Al₁₂Si₆O₃₆S₂₋₄</td>
<td>640</td>
<td>S, CT</td>
</tr>
<tr>
<td>Manganese Blue</td>
<td>Barium manganate on a barium sulfate base</td>
<td>Ba(MnO₄)₂+BaSO₄</td>
<td>750</td>
<td>LF</td>
</tr>
<tr>
<td>Manganese Blue/Titanium white</td>
<td></td>
<td></td>
<td>500 720</td>
<td>CT, LF</td>
</tr>
<tr>
<td>Monastral Blue</td>
<td>copper(II) phthalocyanine</td>
<td>C₃₂H₁₆N₈Cu</td>
<td>600 770</td>
<td>CT, LF</td>
</tr>
<tr>
<td>Monastral Blue/Titanium white</td>
<td></td>
<td></td>
<td>540 714</td>
<td>CT, LF</td>
</tr>
<tr>
<td>Prussian Blue</td>
<td>Ferric hexacyanoferrate</td>
<td>Fe₅(CN)₁₀(H₂O)₅</td>
<td>560 680</td>
<td>IV CT</td>
</tr>
</tbody>
</table>

*LF – ligand field transition; CT – charge transfer transition; IV CT – intervalence charge transfer transition

The depth of color is related to the molar decadic absorption coefficients of transitions in the visible region of the spectrum and also to the dimensions of the pigment dimensions.

On the basis of the chemical formula, one can reasonably assume that the transition – metal ions: copper, manganese, cobalt, iron are the active optical centers, the interpretation of the spectra being dictated by the spectroscopy of these metals in a solid matrix.

The studied blue pigments, illuminated with light of the same spectral compositions, showed different DRS spectra, so the metamerism was high (Figure 3).
Fig. 3 – Diffusive reflectance spectra (DRS) of some traditional and modern blue pigments (1 – azurite, 2 – manganese blue, 3 – cerulean, 4 – Monastral blue, 5 – cobalt blue, 6 – ultramarine, 7 – Prussian blue).

Cerulean blue and cobalt blue have a high reflectance of the red radiation. The painting surfaces are observed as having a magenta nuance.

To minimize metamerism phenomenon were prepared mixtures with titanium white. The optimum mixture contained $10^{-2}$ M blue pigment (Figure 4).

Fig. 4 – DRS spectra of pigment mixtures containing $10^{-2}$ M blue pigment (1 – Azurite/ Titanium white, 2 – Monastral blue/ Titanium white, 3 – Manganese blue/ Titanium white, 4 – Cobalt blue/ Titanium white, 5 – Prussian blue/ Titanium white).

The Kubelka – Munk function was affected by the presence of titanium white and there was visible shift of DRS spectra toward a lower wavelength. This fact
suggests a distortion of the symmetry of cation environment and charge transfer involving cluster-like species.

The DRS spectra of azurite/titanium white and manganese blue/titanium respectively evidenced almost the same values for the K – M function (Figure 5).

Fig. 5 – Comparison of Kubelka–Munk functions of two compatible pigment mixtures.

5. CONCLUSIONS

DRS can offer information on the electronic absorption spectra of the pigment samples, when they are realized in adequate dilution of the pigments in standard substance. It is a good method for the investigation of the constitutive materials of old paintings.

Also DRS can be used for establish the mixtures or actually synthetic pigments or colorants for substitution the old pigments, resulting optimum recipes for surfaces painting restoration with blue pigments.

By mixing modern blue pigments with titanium white it is possible to obtain pigments azurite imitative retouching.

The best modern pigment for the original pigment azurite is manganese blue. Prussian blue and Monastral blue are acceptable for matching traditional azurite.

REFERENCES