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Study of Photodestruction of Pigments of Various Chemical Composition Under Laser Exposure

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Abstract
This article presents an overview of current research on the photodegradation of pigments of various chemical compositions under laser irradiation. The main groups of pigments-organic, inorganic, and those containing photocatalytically active components and their sensitivity to light and laser are examined. The mechanisms of degradation, including thermal and photochemical effects, as well as combined effects, are discussed. Modern methods for studying photodegradation are presented: X-ray diffraction, microscopy, spectroscopy, colorimetry, and controlled laser irradiation.

Keywords: Photodestruction of pigments, laser action, organic pigments, inorganic pigments, TiO_2, destruction mechanisms, spectroscopy, laser tattoo removal.

Introduction

The scientific novelty of the article lies in the systematic analysis of photodestruction of pigments of different chemical compositions under laser irradiation, combining the classification of pigments, destruction mechanisms, and modern experimental research methods.

Pigments are insoluble coloring agents widely used in painting, inks, monument restoration, the tattoo industry, and other fields. Their chemical composition can vary greatly, from simple inorganic metal oxides to complex organic dyes. When exposed to light, and especially laser radiation, pigments undergo a variety of changes: color change, alteration of crystalline structure, bond breakdown, formation of new phases, and degradation products. Pigment photodegradation processes are relevant in several contexts: cultural heritage restoration (where lasers are used for cleaning and conservation), tattoo removal (where lasers are used to destroy pigment in the skin), as well as general photochemistry and photothermal effects on materials.

Modern research shows that laser irradiation can alter the crystalline phase or chemical composition of a pigment even at the superficial, near -nanometer scale. For example, for the pigments HgS (Chinese red) and white lead pigment ($2 PbCO_3 Pb (OH_2)$), laser irradiation has been shown to cause structural and compositional changes, despite the traditionally high stability of such inorganic compounds [1].

Understanding the photodegradation patterns of various pigment types (organic and inorganic, with and without photocatalytically active components) is of great practical importance: for ensuring safety during laser cleaning, assessing the durability of paint coatings, optimizing removal procedures, and identifying potential toxic degradation products during laser exposure. For example, a review of current literature highlights significant gaps in knowledge regarding pigment degradation products during laser irradiation [2].

In this regard, the purpose of this article is to systematize the current state of knowledge on the photodestruction of pigments of various chemical compositions under the influence of lasers, to evaluate the mechanisms, research methods and practical aspects.

Before examining the mechanisms of photodegradation in detail , it's important to systematize existing information about the pigments themselves. Their chemical composition, organic or inorganic nature, and the presence of photocatalytically active components all determine their sensitivity to light and laser irradiation.

Based on their chemical composition, pigments are usually divided into two main groups:

1. Inorganic pigments are pigments based on metallic compounds, oxides, sulfides, complex oxides, etc. They usually have high thermal and light resistance.

2. Organic pigments - based on carbon-containing molecules (azo, anthra, phthalocyanines , etc.). They usually have greater brightness and color saturation, but are often inferior to inorganic pigments in terms of lightfastness and heat resistance.

In addition, there are subgroups: pigments with photocatalytic activity (for example, containing $TiO2$), effect pigments (pearlescent, metallic), special functional pigments.

Inorganic pigments generally exhibit high lightfastness, good resistance to environmental influences, and a relatively lower susceptibility to degradation under the influence of light. For example , in one from scientific articles It is noted : “Most of the technically relevant pigments consist of particles … The most permanent of pigments are inorganic synthetics, … and of those that deteriorate, the fastest fading materials are organic” [3] . Pigments based on iron oxides, ultramarine and other synthetic inorganic pigments have excellent lightfastness.

However, even inorganic pigments can be damaged by laser irradiation: for example, in a study of HgS (Chinese red) and white lead pigment, changes in the crystalline phase or composition were recorded under laser irradiation [1].

Organic pigments typically exhibit higher sensitivity to light, ultraviolet, and laser radiation. One scientific paper states that photolysis of organic pigments (particularly in tattoo inks) can produce toxic degradation products [2]. When analyzing lightfastness, it is stated: " organic pigments offer high chroma ... They are more susceptible to solvents, ultraviolet light, and weathering" [4]. A study using laser irradiation of yellow pigments (PY14, PY74, PY65) with TiO_2 showed that the composition affects the rate of destruction [5].

When laser processing pigments, the following points are important:

1. Energy density, pulse mode, and wavelength all influence the degree of impact. A study using HgS / Pb -white lasers found changes at the surface nanometer level [1]. The presence of photocatalytic components (e.g., TiO_2) increases the likelihood of photochemical degradation under laser irradiation. Organic pigments have a higher risk of forming degradation products under laser and/or solar irradiation.

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Table 1 - Comparison of pigment groups by sensitivity

Group of pigments	Typical representatives	Lightfastness level	Sensitivity to laser exposure	Comments
Inorganic	Fe_2O_3 ("mars -red"), TiO_2 , ultramarine	High - good stability	Low → moderate (under normal conditions)	But they can change at high laser doses.
Organic	Azo -pigments, phthalocyanines , dioxazines	Moderate → low.	High → very high	Higher risk of decay products, toxicity.

Thus, the following key observations can be made:
- classification into inorganic and organic pigments is important because the chemical nature determines the resistance to light and laser;
- inorganic pigments are in many cases more stable, but do not guarantee complete insensitivity to laser exposure, especially at high energy densities;
- organic pigments require increased attention during laser treatment (for example, in restoration or tattoo removal), since they can deteriorate more quickly and form unwanted products;
- when using laser treatment (as a special type of photo/ thermal effect), it is important to take into account the composition of the pigment, the presence of photocatalytic components, the wavelength and energy of the laser.

Next, we will examine the key mechanisms by which laser radiation promotes pigment destruction. Based on literature data, we have identified three main pathways: thermal (photothermal), photochemical, and mechanical (or a combination of these) - often acting in concert.

1. Photothermal mechanism. Laser radiation is absorbed by the pigment or binder and converted into thermal energy, causing local heating, thermal stress, phase transformations, melting, or evaporation. For example, in a study with Pb_3O_4 (red lead pigment), it was shown that when irradiated with a 532 nm laser with a density of ~5.1×10^4 W/cm², the transformation to β- PbO begins at a local temperature of about 500 °C [6]. In a scientific review of remote Raman spectroscopy of historical paints, it was shown that when using a 780 nm laser with high intensity and a long irradiation time, changes are observed, which the authors associate with the accumulation of heat (heat accumulation) in the pigment [7]. Thus, for a pigment or coating, it is important how efficiently heat is dissipated: low thermal conductivity, high radiation absorption capacity, and prolonged irradiation increase the risk of thermal destruction.

2. Photochemical mechanism. Laser exposure can also trigger electron excitation processes, the formation of free radicals, and photocatalytic reactions, which is especially relevant for pigments with photocatalytically active components. In a study with yellow pigments (Pigment Yellow 14, PY74, PY65) and TiO 2 showed that laser irradiation at 532 nm changes the morphology and structure, and forms volatile degradation products, with the authors attributing this to the photocatalytic activity of TiO 2 [5]. Also, in work with pigments at 780 nm , it was noted that organic pigments change faster than some inorganic pigments, which may be evidence of photochemical (and not just thermal) processes [7]. It is important to note that the photochemical

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mechanism can operate even without significant heating if the pigment or binder is capable of generating radicals, oxidizing under light, or reacting upon excitation.

3. Combined and mechanical effect. In practice, laser exposure leads to a combination of effects: in addition to heat and photochemistry, microstructural damage, cavitation, shock waves (especially with pulsed lasers), and mechanical destruction of the binder or pigment capsules are possible. A review on tattoo removal noted that after laser treatment of the pigment, fragmentation of the particle, the formation of small particles, and changes in agglomeration are possible, reflecting mechanical destruction [8]. In a study on the cleaning of archaeological pigments, it was found that lasers with different wavelengths (532 nm and 1064 nm) produce different levels of damage and mechanical changes [9].

Therefore, when laser cutting, it is important to consider not only the thermal or photochemical effect, but also the potential mechanical consequences, especially when working with supports, paint layers, or fabric/sculpture materials.

Table 2 - Summary of the mechanisms of photodestruction of pigments under laser exposure

Mechanism	Main route of exposure	Typical manifestations	Factors that enhance the effect
Photothermal	Absorption → heating → thermal destruction	phase change, melting, discoloration, cracks	high absorption, low thermal conductivity, long-term irradiation
Photochemical	Excitation → radicals / photocatalysis → destruction	decomposition of molecules, formation of volatile products	the presence of a photocatalytic component (TiO_2), organic pigment
Combined / mechanical	Thermal + photochemical + pulse/mechanical effects	fragmentation, change in particle agglomeration, shock waves	pulsed mode, ablation, weak binding

The mechanisms of laser-induced pigment photodegradation are multifactorial and interrelated. Understanding which mechanism predominates in a particular system (pigment + binder + laser parameters) allows one to select optimal exposure parameters or anticipate the risk of damage. When working with layered paints, artwork, tattoos, or industrial coatings, it is important to consider the following: the pigment's spectrum and absorbance, the thermal conductivity/heat capacity of the system, the presence of photoactive components (e.g., TiO2), laser parameters (wavelength, fluence, pulsed/ non-pulsed, exposure time), and the binder/environment conditions (humidity, substrate, agglomeration).

Studying laser-induced pigment photodegradation requires a comprehensive approach, as degradation processes can involve thermal, photochemical, and mechanical effects. Modern methods allow for the detection of both structural and chemical changes, as well as quantitative assessment of pigment color and morphology changes.

1. X-ray diffraction (XRD). XRD is used to detect phase changes and the crystalline structure of pigments after laser irradiation. Example: when studying HgS and Pb_3O_4 under Nd:YAG laser irradiation, the formation of new phases and local changes in crystallinity were detected [1]. XRD

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allows for the recording of $\alpha \rightarrow \beta$ phase transitions, the formation of metal oxides, and the degradation of inorganic pigments.

2. Microscopy and microanalysis (SEM, TEM, EDX). These methods provide information on the morphology, size, and agglomeration of pigment particles. EDX allows one to determine the chemical composition and identify degradation products. For example, after laser treatment of PY14 + TiO_2 , particle fragmentation and morphological changes were observed [5]. SEM allows one to observe cracks, bubble formation, and other mechanical effects.

3. Spectroscopic methods (FTIR, Raman , UV- Vis). FTIR is used to evaluate changes in molecular structure, the rupture of chemical bonds, and the formation of degradation products. Raman spectroscopy allows for non-destructive examination of crystalline and organic pigments and the determination of structural changes after laser irradiation. UV- Vis spectroscopy records changes in the absorption and color of the pigment. Example: changes in the spectrum of carminic acid after VIS and laser irradiation revealed the formation of free radicals and molecular degradation [10].

4. Colorimetry and ΔE measurement. Colorimetric methods allow us to quantitatively evaluate the change in pigment color after laser exposure. ΔE (color difference) is a simple indicator of photodegradation. Example: for organic pigments in tattoo inks, ΔE exceeded 10 units under a 532 nm laser, indicating noticeable changes [11].

5. Controlled laser action. Laser parameters (wavelength, pulse/ non-pulse , energy density) are carefully adjusted to assess damage thresholds and the mechanism of destruction. Example: in remote Raman spectroscopy, a 780 nm laser was used to assess the safe threshold for photodestruction of pigments [7].

6. Additional methods:

- thermography records a local increase in temperature during laser exposure;
- chromatography and mass spectrometry for organic pigments allow us to identify degradation products and assess toxicity;
- AFM microscopy studies nanostructures and pigment surfaces after irradiation.

Table 3 - Methods for studying photodestruction of pigments

Method	Main purpose	Type of information	Example of application
XRD	Phase changes, crystal structure	Crystallography	HgS and Pb_3O_4 under laser
SEM / TEM / EDX	Particle morphology, chemical composition	Microstructure, elemental analysis	PY14 + TiO_2
FTIR / Raman / UV-Vis	Molecular and structural changes	Chemical structure, spectra	Carminic acid, VIS and laser irradiation
Colorimetry (ΔE)	Color change	Visual effect	Organic tattoo -pigments
Controlled laser exposure	Assessment of damage thresholds	Mechanisms, safe levels	Raman spectroscopy 780 nm
Chromatography/MS	Destruction products of organic pigments	Composition and toxicity	Organic pigments
Thermography	Local heating	Temperature distribution	Binder + pigment in pulsed laser

Experimental methods allow for a comprehensive assessment of pigment changes under laser irradiation. The combination of radiography, microscopy, spectroscopy, colorimetry, and controlled lasers enables understanding and quantification of both thermal and photochemical effects. These methods also help identify degradation products, assess their potential toxicity, and develop safe approaches for the practical application of lasers in restoration, industry, and cosmetology.

Thus, photodegradation of pigments under laser irradiation is a multifactorial process, dependent on the pigment's chemical composition, structure, binder, laser parameters, and environmental conditions. Organic pigments exhibit higher sensitivity, but inorganic pigments cannot be considered completely stable either. The presence of photocatalytic components (e.g., TiO_2) can accelerate degradation.

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