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An analytical study on an early twentieth-century Italian photographs collection by means of microscopic and spectroscopic techniques

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ABSTRACT

Italian photographs, dated between 1890 and 1930, on simple or treated paper support, chosen to be faithful to Italian photographic tradition of those times, were studied with non-invasive techniques. A first investigation by optical microscopy in reflected light put in evidence the surface peculiarity of each different photo types, characteristics and deterioration of the fibres and vegetable biodeteriogens morphology. The study of coatings and supports composition, carried out with Fourier transform infrared micro-spectroscopy in attenuated total reflectance, allowed to recognise the presence of proteinaceous binder and inorganic salts. Moreover, stereomicroscopy, optical microscopy (in reflected and transmitted light) and scanning electron microscope were used for more detailed study of biodeterioration phenomenon. These instrumental techniques have been useful to evaluate cause of chromatic differences on the surface, allowing the identification of different fungi species, and, particularly, a class of them never documented on photographic materials has been detected. Materials identification, deterioration knowledge and formulation of hypothesis on the causes of deterioration are of primary importance to act the better choice for adequate preservation and conservation process.
This study shows how non-invasive techniques are completely applicable on photographic materials, field in which diagnostic analyses are still not fully overworked.

1. Introduction

Between 1820 and 1840, many experiments were done from England to France trying to capture images of reality and keep them on a support, bringing scientific talents to realize the very first kinds of photograph pictures. In Paris, in 1839, there was the first official announcement about the Daguerre's technique: the Daguerreotype. From that many other ways to capture images have been created, bettering times of exposition and quality of materials and final products.

When, in 1850, the first photographic technique on paper became very widespread, it was improved with an additional compound: the binder. The use of binder became necessary to protect silver particles from air pollution or substances present into adjacent materials, from the residual of fixing image process and UV rays, saving the images from oxidation and any other kind of deterioration processes [1].

In other photographic techniques, like heliography, calotype, daguerreotype and ambrotype, silver formed the image; but in the first times there were also stamp processing without silver in which were used platinum or iron salts [1–5].

In simple salted papers, used from 1840, the paper support was impregnated in a solution with sodium chloride and then sensitized with silver nitrate, without using binders [6].

The innovating addition of the binder during the salting process had two different version: starch salted paper with a further addition of rice or potatoes starch solution (2% concentrated) and gelatine salted paper made using a gelatine solution (from 1% to 4% concentrated). The two different kinds of bonding agent gave different tones to the image: violet tones for starch and red tones with gelatine. Albumen, used from 1850, was at first addicted to the salt bath, then, from 1860, it becomes a binder, in which the photosensitive substance reacts and silver particles are kept [6]. Silver grains stay at the surface of the support giving a more contrasted image. These prints are composed by two layers but generally they had another support, because the thin one made of paper tended to crumple when protein binder contracts during drying. Albumen, to be used as a binder, needs a specific treatment of denaturation: whipping and fr'othing the egg white to obtain a homogeneous phase easily placed on support arises.

Every albumen protein denatures irreversibly during treatments that did not consist in a simply water evaporation, but includes also alcohol baths, high temperature and high pressure to obtain glossier stamps. A process used to increase superficial gloss but which alters material properties in albumen photographs is fermentation. It causes irreversible changes in the structure of organic materials when, in

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condition of high humidity and high temperatures, they are exposed to microorganisms and their specific enzymes [7–10].

In 1890, a new kind of photographs born: the aristotypes. Prints contain gelatine as binder, the image forming is direct and the emulsion is isolated from the support by a layer of barium sulphate [6].

First gelatine emulsions were used on glass. Then this emulsion on paper and plastic supports is found, the image was obtained in two different ways: at first with direct contact between negative and positive plates (or papers), then with chemical development [1]. Gelatine is stable, but very sensitive to high temperature and high humidity ranges. Its characteristics are suitable for a photograph use, it is rich of sulphur and increases the silver halide's photosensitive, it is also hydrophilic and guarantees a very good penetration in the treatment baths (optimum for high image quality) [7].

Collodion is a polymer with bonds between hydroxyl groups of cellulose and nitric acid (nitric ester of cellulose) at high esterification degree. Collodion preparation was known before 1870, but in this year, at first time, it is been used on paper to obtain positive images. Collodion needs very quick times of use, if it remains exposed it solidifies for solvent evaporation, it loses porosity preventing treatments, become inflammable, low soluble in water, sensitive to alcohol, ether and organic solvents [11]. Before spreading on the support, collodion solution must be kept far from the light and into a sealed box.

A barite layer was interposed between the binder and the support, to warrant a good protection from impurities of paper, better adherence of the emulsion and better image definition, separating the image layer from the paper's fibres.

All problems of collodion emulsion in the range between preparing and using times were overcome when gold salt, sodium chloride, silver nitrate, citric acid and glycerine have been added to the emulsion. The pre-treated paper was very easy to use, more stable, more definite lights and shades and careful details [10].

Different photo types are subject to characteristic deterioration phenomena which are due to chemical nature of various constituents and their interaction with environmental conditions. For example, first salted papers were more susceptible to deterioration agents, there was not any protection for support and silver so paper, damaged by UV rays, becomes more fragile, faded and acid [12].

Albumen, on the contrary, was susceptible to cracking, lost clearness of the image and yellowing, deterioration effects which take potential beginning in the making of the binder in itself. In particular *cracking* is the formation of superficial cleavages and it depends on quick variations of humidity [13]. Yellowing depends on: reaction between proteins and sugars [14], presence of sulphur, presence of silver/protein complexes and long exposition to UV rays [15,16].

High humidity of conservation environment is most common cause of deterioration for gelatine prints.

Gelatine hydrophilicity brings important changes as softening, and increase of solubility. When humidity falls, gelatine suffers a quick hardening, eventually detachment from support and surface variations of opacity and brightness [3].

In spite of collodion prints are generally stabiles, humidity causes surface cracking and nitrogen oxide release, which breaks cellulose chains in the paper support. Other kind of deterioration concerns silver particles if photo types are exposed to oxidant agents which cause, by an oxidation then a reduction of silver, a production of colloidal silver that generates the silver mirror. Gelatine is particularly affected by this kind of phenomenon because permits the ionic migration of oxidised silver because of its hygroscopy [14]. The variety of constituent materials of photographs composes a very productive soil for many kinds of microorganism, which never attack singularly and on a circumscribed zone, but they generally operate in synergy, taking advantages each other for the presence of other ones [17]. Fungi and bacterium, that can easily come from the atmosphere, are the most dangerous microorganisms for the photographs, especially in environmental conditions favourable for their proliferation [18].

In particular, fungi are pluricellular microorganisms, heterotrophic, eukaryote, structured in hyphae, which compose the vegetative body of the mushroom in itself, called mycelium.

They are aerobic organisms, generally saprophyte and most rarely parasitic or symbiotic; they have a fundamental rule in organic compounds decomposition and in oxidative fermentation processes of carbohydrates in which organic acids (citric, oxalic, fumaric, succinic) are produced through the activity of Aspergillus, Mucor, Penicillium and Rhizopus. Most of species are acidophilic, and living better at a pH less than 6.

Fungi nutrition depends on the presence of water, whether in environmental humidity degree or in material intrinsic humidity degree. Organic acids, triglycerides, carbohydrates, proteins and amino acids, hydrocarbons, hemicelluloses and lignin are potential sources of carbon and nitrogen, nourishing for most of fungi species.

Deterioration action due to fungi nutrition is the production of specific acid enzymes, depending on surface composition and mycelium extension, which causes chemical, physical and mechanical damages [19].

The purpose of the present work is to recognise composition, and deterioration phenomena of ancient Italian photographs located in Photographic Archives of Musei Civici, Reggio Emilia (Italy). From a chemical point of view, an integrated analytical approach based on the use of non-invasive techniques is demanded to describe different photographic techniques, the specific causes and effects of deterioration for every kind of materials. In particular, the identification of the materials is a fundamental step to individuate the right way to preserve photographs and, when necessary, to act an adequate restoration plan. In this sense, the precise knowledge of substances, causes and implicated processes guarantees an appropriate and conscious approach, decisive for the good recovery, the protection and the conservation [20–25].

2. Experimental

2.1. Materials

Materials studied are forty Italian photograph types on paper support, located in the Photographic Archive of Musei Civici in Reggio Emilia (Italy), dated between 1890 and 1930. Prints present different characteristics on the surface, and some of these have another support of paperboard under the paper one. Moreover, a print, from a personal collection, having interesting chromatic spots on the surface, has been studied.

2.1.1. Instruments and methods

2.1.1.1. Optical microscopy. The microscope investigations were carried out with an Optical Microscope Carl ZEISS (Germany) — model Axiotech, equipped with CCD, which permits applications in reflected and transmitted light (magnification up to 1000). Magnifications were 10×, 20×, 50× and 100×, while the sources for reflected light were 6 V 30 W halogen light or 12 V 100 W halogen light; and for transmitted light there was a 6 V 30 W halogen light. The microscope Cameras for 35 mm and/or large frame was a MC 80 DX.

2.1.1.2. Stereo microscopy. A visual analysis of the photograph surface was carried out by means of an OPTIKA SZM stereo microscope.

2.1.1.3. Micro-Fourier transform infrared spectroscopy (FTIR). Micro-FTIR spectra were taken in attenuated total reflectance (ATR) mode employing a ThermoNicolet “Continuμm” Nexus line micro-spectrophotometer, equipped with a mercury–cadmium–telluride (MCT) detector. A micro-slide-on ATR silicon crystal directly connected to the objective has been used. Infrared spectra were recorded in 4000–650 cm^{-1} range, resolution 4 cm^{-1} and 120 scans.