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Effect of aging in starch based adhesives, studied using second harmonic generation imaging microscopy

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Many valuable works of art on papers or even whole books probably would have been entirely lost without a skillful restoration. In paper conservation, adhesives are used to consolidate, fixing, mending, filling of losses, lining, matting and framing or to provide binders, glazes, and varnishes. Specifically, weak or brittle papers or sheets are commonly conserved by backing (lining) them with another sheet of paper. The lining is usually adhered with an adhesive based on starch. The basic principle of lining is minimal intervention. In particular, the adhesive should create less impact on the paper, physically as well as chemically. The lining glue selected should further demonstrate long-term stability and aging characteristics. Stability may be judged by natural or accelerated aging and consequent analysis. The results of such tests and their evaluation are of great assistance in making a final decision on the most appropriate restoration treatment.

Nonlinear imaging microscopy (second harmonic generation (SHG), third harmonic generation (THG) and two photon excited fluorescence (TPEF)) is already well established technique for biological imaging. Recently THG and TPEF have been employed for Cultural Heritage (CH) studies providing exact thickness determination and compositional identification of fresh and aged varnish protective layers, pigments and corrosion layers [1]. In contrast to TPEF, which relies on nonlinear absorption, SHG and THG rely on nonlinear scattering and, thus, are regarded as minimally invasive imaging techniques. While THG primarily appears where there is a change of refractive index, SHG is strong in non-centrosymmetric materials and originates from laser induced 2^{nd} order polarization. The SHG signal is sensitive to the incoming excitation polarization and to the SHG active structures architecture. By rotating the axis of linear polarization reaching the sample and by recording the dependency of the detected SHG signal, it is possible to gain structural information unreachable by common intensity only SHG imaging [2]. Polarization sensitive SHG (PSHG) imaging has been used lately to characterize the molecular architecture of main endogenous sources of contrast in tissues [3,4] and in starch [5].

Here, we use PSHG to compare naturally aged (~7 years) starch based adhesives (flour pastes and starch pastes) samples, with fresh ones. We found that in aged glues, the starches' SHG angle, ϑ is shifted to higher values, in comparison to the fresh granules. Modifications due to aging on starch, altered ϑ, thus the minimally invasive PSHG optical technique was able to recognize aged from fresh glues.

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