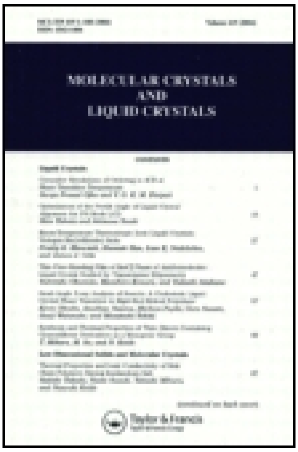

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A New Non-Destructive Method to Differentiate In Situ Marble from Gypsum and $CaCO_3$ from Inversion of Gypsum; Use of Liquid Crystals

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A New Non-Destructive Method to Differentiate In Situ Marble from Gypsum and $CaCO_3$ from Inversion of Gypsum; Use of Liquid Crystals

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Based on our previous work, with which it was proved that the reflected light (wave length) from cholesteric liquid crystals also depends on the adsorption properties of the surface of their supports, we used them to differentiate gypsum from marble and $CaCO_3$ (from inversion of gypsum) with success. This is interesting for the study of the preservation and restoration of ancient monuments or new buildings. Thus, a new non-destructive method to be used in situ has resulted.

Keywords: sorption, marble, Gypsum, differentiation, restoration.

INTRODUCTION

For preservation and restoration purposes, a method is needed to reveal, in situ, the presence of gypsum, which is formed by the action of the pollutants SO_2 + SO_3 with humidity on the surfaces of marbles or other calcereous stones of ancient monuments or new buildings which are protected from rain water (on surfaces that they come in contact with rain water gypsum is eliminated because of its solubility in water). Two qualitative and one semi-quantitative non-destructive method have been used to date:

i. An indirect method uses the fact that where gypsum is formed, suspended particles are coagulated which color the surfaces black (C) or red (Fe_2O_3).
ii. Another qualitative method is the use of radizonic natrium or cinalizarin etc, but the coloring of the surface cannot be easily eliminated.
iii. A semi-quantitative method is our "pin probe method."[1,2]

Besides the need to reveal the presence of gypsum in situ with a non-destructive

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method, a new need arises from the application of our new method for the inversion of gypsum into $CaCO_3$[3-5], i.e., the possibility to certify this inversion by differentiating in situ marble from $CaCO_3$ (and the latter from gypsum). Until now this differentiation was not the object of any work. To do both, we used liquid crystals, the reflected light band from which also depends on the adsorption properties of the surface of their supports, as we found in previous work.[6-9] Precisely as it is known, the reflected light band by the cholesteric liquid crystals is usually shifted to longer wave-lengths as the temperature decreases[10-12] or the applied pressure increases[13-16]; electric[10-12,17] or magnetic[10-12,17,18] fields and small quantities of impurities[19] also change their color. This color change is the result of the influence of the above mentioned parameters upon the pitch.[10-19] The sensitivity of the color change is extremely strong in the neighborhood of a cholesteric-to-smectic phase transition.[11,16]

If we used solid sorbents, with high physical adsorption properties, as supports for cholesteric liquid crystals, the reflected light of the latter were influenced[6-9] since the sorbents act on the sorbates with strong mechanical and/or electrical forces due to applied pressure[13-16] or an electric field[10-12,17] respectively by the sorbents. This explanation is further studied. Thus, we differentiate in this way γ_1-Al_2O_3 from γ_2-Al_2O_3 electrolytically prepared,[6,7] γ_1-Al_2O_3 prepared with different current densities,[6,7] chemically and electrolytically prepared ZnO and Fe_3O_4,[6,7] copper mechanically cleaned and electroplated,[6,7] and nickel electrodeposited with different orientation.[9] The validity of a rectilinear relationship between the adsorption properties of the support and the shift of the reflected wavelength from the cholesteric liquid crystals spread on their surface was also shown.[8]

EXPERIMENTAL

Origin, Shape and Dimensions of Marble Specimens

The marble used for the laboratory experiments was from the same quarry from which the Acropolis monuments are constructed. The dimensions of the specimens were 2cm X1cm X0.3 cm, suitable to fit the spectrophotometer holder.

Procedure

i. Laboratory measurements. Three types of specimens were used: marble, sulfated marble and sulfated marble after inversion of the gypsum into $CaCO_3$. The marble specimens were degreased before treatment with liquid crystals.

The sulfated marble was made by exposure of marble to an environment of 50% SO_2 and 50% air saturated with water vapor at 25°C for 8 days. In this way, gypsum on the surface of the marble was prepared (see kinetics and mechanism of sulfation in References 20–25).

The sulfated and inversed specimens were made from sulfated specimens after total inversion of gypsum into $CaCO_3$ by immersion in a 0.3 M K_2^{2+} CO_3^{2-} solution at 20°C during 3 months (see kinetics and mechanism of inversion in References 3–5).

On the surface of six of the three types of specimens a diethylether solution of a 10% mixture of cholesteric liquid crystals (1:4 mixture of cholesteryl-4-carbomethoxyoxybenzoate and cholesteryloleylcarbonate) was spread.

Each specimen was placed in the holder of the spectrophotometer and its diffuse reflectance spectrum[6–9] was obtained at 25°C in the visible portion of the spectrum. The same procedure followed at 26°C, 27°C, 28°C and 29°C to reveal the temperature where the differentiation was more pronounced.

Photographs were also taken of the three types of specimens with the liquid crystal mixture on them.

On the visible diffuse reflectance spectra, the wavelength of the peaks was measured for the six specimens of the same type and at the same temperature; the mean value (λ) was found in nm. The same procedure was followed for the various temperatures. From these mean values the peaks (λ') of the liquid crystals mixture on a blackened glass plate for the different temperatures was substracted (see detail in References 6–9).

ii. Measurements in situ. On the surface of the marble of the Acropolis monuments that came in contact with rain water and after a recent rain (the gypsum was totally washed off) and drying with infrared radiation, the solution of the cholesteric mixture of liquid crystals was sprayed. The colors were observed and photographed. The same was done on a surface protected from rain water where gypsum was present, after removing the coagulated suspended particles by using sipiolithe paste with water saturated with SO_4^{2-} in order not to eliminate gypsum (the presence of gypsum was identified by XRD in a small sample) and on a sulfated surface after inversion of gypsum into $CaCO_3$ by spraying the surface several times with a solution of 0.3 M K_2^{2+} CO_3^{2-}. After drying the colors were observed and photographed.

RESULTS AND DISCUSSION

i. The results of the laboratory experiments are shown in Table I and in Figure 1. From Table I and mainly from Figure 1 the differentiation of the three types of specimens is observed. The differentiation is more pronounced at lower temperatures as expected.[6–9] The marble (aged $CaCO_3$), having lower adsorption

TABLE I

Temperature (°C)	25	26	27	28	29
Type of specimens		λ (nm) mean values of 6 measurements			
Marble	599	489	441	422	411
$CaCO_3$ from inversion	664	510	453	430	415
Sulfated marble	724	556	476	438	422
Black glass (λ')	515	451	423	411	406
Type of specimens			λ-λ' (nm)		
Marble	84	38	18	11	5
$CaCO_3$ from inversion	149	59	30	19	9
Sulfated marble	209	105	53	27	16

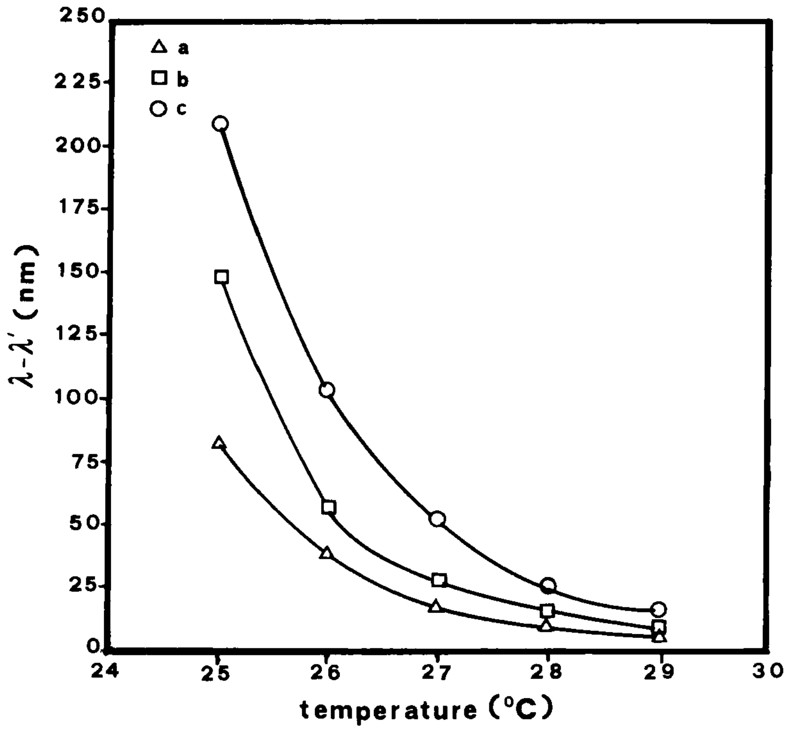

FIGURE 1 λ-λ' vs temperature. Substrate: a) Marble; b) $CaCO_3$ from inversion of gypsum; c) gypsum.

properties, shifts the wavelength less than the recently produced $CaCO_3$ by inversion (different microstructure); gypsum shifts the wavelength more.[6]

ii. Results in situ. The results in situ are a little different. The differentiation in color between bare marble and $CaSO_4 \cdot 2H_2O$ from inversion is very clear. The differentiation between marble and $CaCO_3$ is also clear, but between gypsum and $CaCO_3$ from inversion the difference is less clear than in the laboratory. If the experiments were repeated without removing the coagulated suspended particles, the differentiation could be observed in spite of the different initial color of the gypsum. This is also due to the increased adsorption properties of the particles. The cholesteric mixture of liquid crystals can be easily removed by use of diethylether or other solvents.

CONCLUSIONS

From the above mentioned it follows:

1. It is possible, in situ, to distinguish by the difference in color between marble, $CaCO_3$ from inversion of gypsum and sulfated marble with a new non-destructive method using a cholesteric mixture of liquid crystals spread on the surfaces.

2. The method of differentiation is more sensitive between marble and gypsum and between marble and $CaCO_3$ from inversion of gypsum.
3. The differentiation is more pronounced as the temperature decreases.
4. The mixture can be easily removed by diethylether or other solvents.
5. As in previous work, the reflected light band shifts to longer wavelengths as the adsorption properties of the solid supports increase.

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