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Th. Skoulikidis [a] , M. Koui [a] & N. Skotaras [a]
[a] National Technical University, Faculty of Chemical Engineering, Department of Materials Science and Engineering, Athens, 15780, Greece

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Influence of the Sorptive Properties of Zinc Oxide as Support on the Reflected Lightband from Cholesteric Liquid Crystals

TH. SKOULIKIDIS, M. KOUI and N. SKOTARAS

National Technical University, Faculty of Chemical Engineering,
Department of Materials Science and Engineering, Athens 15780, Greece

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In previous work, we have found for the first time that, besides the known conditions that influence the selectively reflected lightband from cholesteric liquid crystals, the physical sorptive properties of their supports also influence the reflected wavelengths. Thus, it was possible to differentiate metal oxides with different microstructures, chemically from electrolytically prepared metals, sulfated from not sulfated monument surfaces, and to identify the fiber texture of nickel electrodeposits. The reflected wavelength was proportional to the sorptive properties of supports.

In the present work, in order to see if the previous findings, especially the quantitative ones, are also valid for other substances, we measured the shift of the wavelength when the liquid crystal mixture covers Zinc oxides prepared by anodic oxidation under different current quantities and by chemical process under different times of immersion in the oxidising bath.

It was found that:

i. The ageing of the oxides leads to a decrease in the reflected wavelength.
ii. The chemically prepared oxides have lower sorptive properties than those electrolytically prepared.
iii. The relation between the physical sorptive properties (mgr/m^2 methylene blue) and the shift of the wavelength is similar to the one valid for aluminium oxides.

Keywords: Cholesteric liquid crystals; sorptive properties of the supports; shift of the reflected lightband

1. INTRODUCTION

In previous work [1–3], we have found for the first time that, besides the known conditions that influence the reflected lightband from the cholesteric liquid crytals (Ch.L.C) (orientation of their molecules on the surface of the supports, contaminations, angle between incident and reflected ray, temperature, pressure, electric and magnetic fields) [4–13] it is also influenced by the physical sorptive properties of their supports, because the sorbents act on the sorbates with big mechanical or/and electrical forces, the very ones that influence the shift, i.e. applied pressure [4–7] or the electric fields [1–3, 8].

Thus, it was possible by the aid of mixtures of liquid crystals to qualitatively differentiate:

i. Metal oxides with different microstructures (Al_2O_3 prepared electrolytically under different current densities or/and current quantities) [1–3].
ii. Chemically from electrolytically prepared metal oxides (Cu, Fe, Ni, Al, Zn) [1–3].
iii. Chemically from electrolytically prepared metals (Cu) [1–3].
iv. Sulfated from unsulfated surfaces of monuments [14].

It was also possible to identify the fiber texture of nickel electrodeposits [15].

It was also found that the most sensitive expression for the shift of wavelength is the difference $\lambda - \lambda'$, where λ is the wavelength at the peak of the diffuse reflectance spectrum for the mixture of liquid crystals on the surface of the sorptive support and λ' the one at the same temperature for the same mixture on the surface of blanckened glass (sorptive inactive).

It was found that between this expression and the sorptive properties (s') of the supports (expressed in mgr/m^2 Methylene Blue) the following equation is valid, for Al_2O_3 prepared under different current densities:

$$\lambda - \lambda' = (30.28 - 0.1T)s' - 121.3 \times 10^6/T^2 + 1351$$

In order to check if this equation in its general form $(\lambda - \lambda')_T = as' + b$ (a and b constant for constant temperature) is also valid for other types of oxides, we measured in the present work the $\lambda - \lambda'$ for the same cholesteric mixture used in previous works, using as its supports Zinc oxides prepared electrolytically and chemically under different conditions.

2. EXPERIMENTAL

2.1. Materials, Shape and Dimensions of the Specimens

There were used two types of Zn specimens:

a) Pure Zn of the industry (Union Carbide) for the preparation of batteries, with the following composition: Zn 99.9%, Pb, Cd 0.1%, Cu, Fe, Mn 0.002%.

b) Galvanized steel sheets from commerce.

The dimensions of the specimens in both cases were 45 x 30 x 0.5 mm.

Also used were: Two Lead electrodes 65 x 50 x 0.5 mm as cathodes, Diethylether, Perydrol pro analysi 30%, alcohol and acetone chemically pure, isolating varnish (air drying varnish 109-000 Golden), isolating Teflon ribbon, NaOH pro analysi 99%, H_2SO_4 95–98%, Phenolphthalein, Methylene Blue. The mixture of cholesteric liquid crystals was 4:1 cholesteryloleyl carbonate ($C_{46}H_{80}O_3$), M.W 681.15 (chemically pure) and Cholesteryl 4-carbomethoxy-oxybenzoate ($C_{36}H_{52}O_5$) M.W 564.81, chemically pure.

2.2. Procedure

2.2.1. Pure Zn Specimens

2.2.1.1. Electrolytically Prepared ZnO

For the preparation of the electrolytically prepared Zn-oxides, a bath of a 0.5 N NaOH solution at a constant 18°C temperature was used.

The Pb cathodes were mechanically cleaned and washed, then they were mechanically abraded to become perfectly flat and thus avoid the different local distances from the surface of Zn anode, which could lead to different local current densitities and different local thicknesses of the ZnO. The distance between the Pb electrodes was 10 cm. The Zn sheets were mechanically polished, washed with deionised water, then with alcohol and ether, and dried. The edges of the sheets were insulated by the insulating varnish and the Teflon ribbon. Each Zn-specimen was placed between the two lead electrodes. After anodizing, the specimens were neutralized, from the NaOH, that had been sorbed from the electrolyzing bath, using a H_2SO_4 solution and phenolphthalein as indicator. The specimens were washed and dried in a flux of air. By this procedure, ZnO with a blue-black color was prepared on the surface of Zn.

2.2.1.2. Chemically Prepared ZnO

ZnO with a 30% H_2O_2 solution was also prepared, washed and dried in a flux of air. The chemically prepared ZnO was white.

2.2.2. ZnO on Galvanized Steel Sheets

Under the conditions of specimens 2.2.1.1, and 2.2.1.2, galvanized steel sheets were anodically and chemically oxidized.

3. MEASUREMENTS AND RESULTS

The following measurements were made on these oxidized specimens:

1) Diffuse reflectance spectroscopy after the mixture of cholesteric liquid crystals was spread on their surfaces and rubbed mechanically in order to acquire the Grandjean microstructure. By a special device, the temperature during the measurements was kept constant. This device was a right hollow parallelepiped in which water of constant temperature was circulated by the aid of a thermostat. The specimens were placed on the metallic surface of this device.
2) On the same type of specimens sorption measurements from a solution of 0.001% of methylene blue [16, 17] were performed.

3.1. Electrolytically Prepared ZnO on Zinc Sheets

3.1.1. Influence of the Ageing of the Oxides

In previous work dealing with the catalytic properties of electrolytically prepared Zinc oxides, it was found that where these oxides act by physical sorption (not by electron exchange) their catalytic properties decrease with the time after their preparation [18]. For this reason the prepared ZnO specimens were left in an exicator at constant temperature and humidity. Measurements of the reflected λ were taken on these oxides at different times (1 hour and 6 days after their preparation) (Preparation conditions: 1.5 A/dm^2, 1.5 h). The results are shown in Figure 1.

It is obvious that the aged specimens provoque a smaller shift of the reflected wavelength of the cholesteric liquid crystals than the younger ones. The real surface of the oxides in several time intervals after their preparation has been measured by BET [18]. In Figure 2 we see a decrease of this surface (cm^2 of real surface/cm^2 of geometrical surface) and consequently a decrease of the physical sorptive properties was also found by direct measurement of the sorption [18].

Thus the following measurements were taken on the specimens immediately after their preparation.

3.1.2. Influence of the Current Density and the Time of Oxidation of the Specimens

It was found that, for the same current density, the time of electrolysis between 1.5 and 3 h do not influence the shift of the wavelength because the

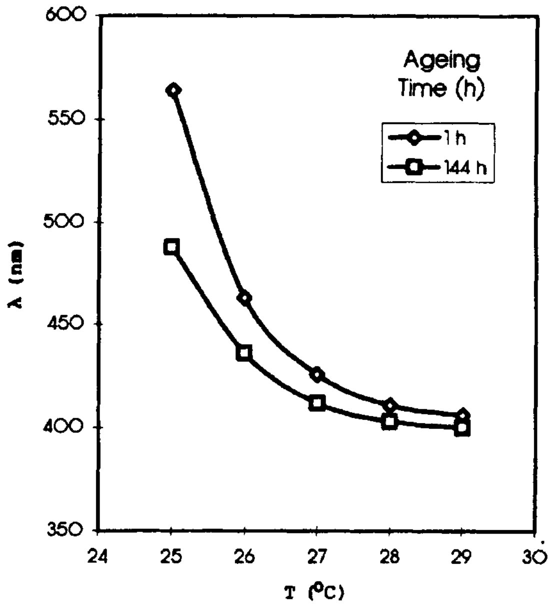

FIGURE 1 Influence of the ageing of ZnO on the reflected wavelength.

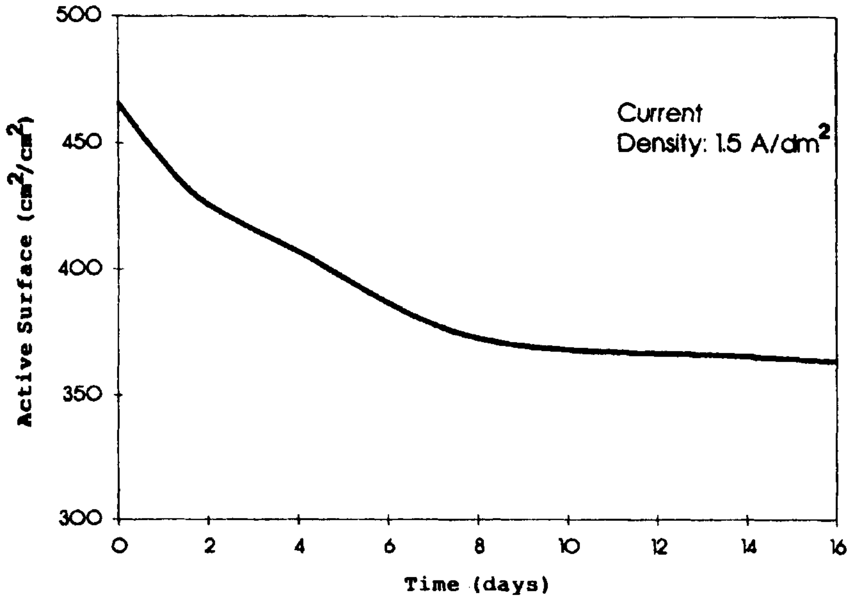

FIGURE 2 Dependence of the real surface on the ageing of the ZnO.

surface sorptive properties of the different thickness of the oxide are the same [18]. The influence of the current density (c.d.) is not appreciable (Fig. 3), but the observation that from the 1.5 A/dm^2 the shift increase up to 4.5 A/dm^2 and then decrease for 6 A/dm^2 is interesting and will be discussed.

3.2. Galvanized Steel Sheets

3.2.1. Influence of the Oxidation Time

As mentioned above, because, the c.d. and the time (current quantity) of oxidation of the preparation of Zinc oxides from Zinc sheets do not influence appreciably the sorptive properties and consequently the wavelength shifting of the cholesteric liquid crystals spread on the Zn-oxides, it was impossible to check the validity of the rectilinear function between sorption and shifting of wavelength (See Introduction). Thus, we thought to use galvanized steel specimens. As it is known, by the hot deep galvanizing, an intermediate zone of a Zn-Fe alloy is formed, with the higher concentration of Fe in its contact with steel and the lowest in its contact with Zn. During anodizing Fe^{2+} diffuse towards the surface of Zn. Thus,

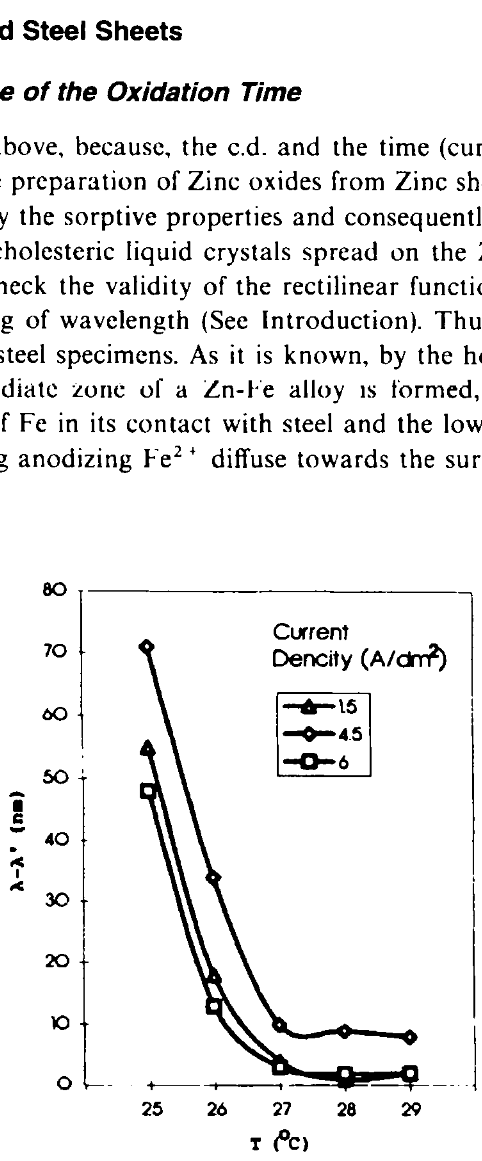

FIGURE 3 Influence of the c.d. on the wavelength shift.

the presence of Fe and consequently of Fe_xO_y as a doping substance in the Zn-oxides could influence the sorptive properties.

3.2.1.1. *Electrolytically Prepared ZnO*

Figure 4 shows that the differences of the reflected wavelength for different current quantities are high, due to the doping of ZnO by Fe_xO_y especially, as it is the rule, at lower temperature. The sorptive properties of the same oxides were also measured for four different times of anodizing 15, 30, 60, and 90 min (Fig. 5).

3.2.1.2. *Chemically Prepared ZnO*

The results are shown in Figures 6 and 7.

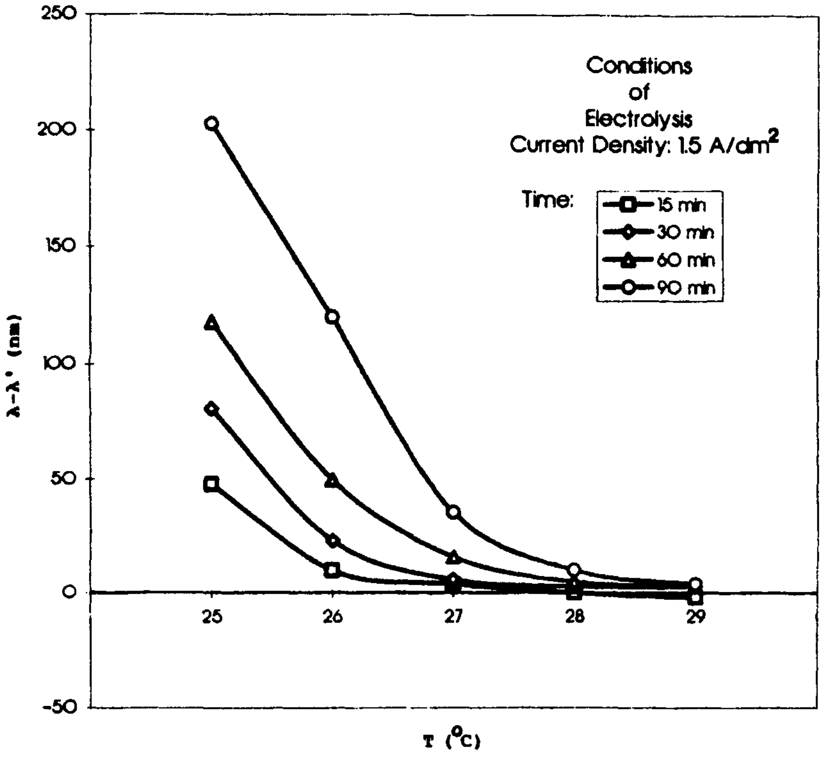

FIGURE 4 Influence of the time of electrolysis.

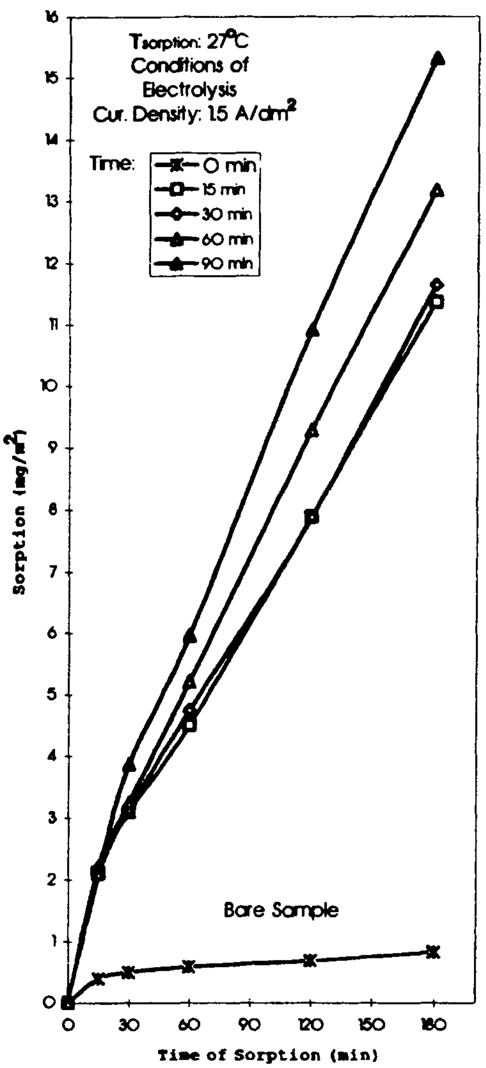

FIGURE 5 Sorption vs time for four times of anodizing.

4. DISCUSSION

The influence of the current density on the reflected wavelength (λ) by the cholesteric liquid crystals spread on electrolytically prepared ZnO on pure Zn, is not appreciable (Fig. 3). But, it was found that the $\lambda - \lambda'$ from

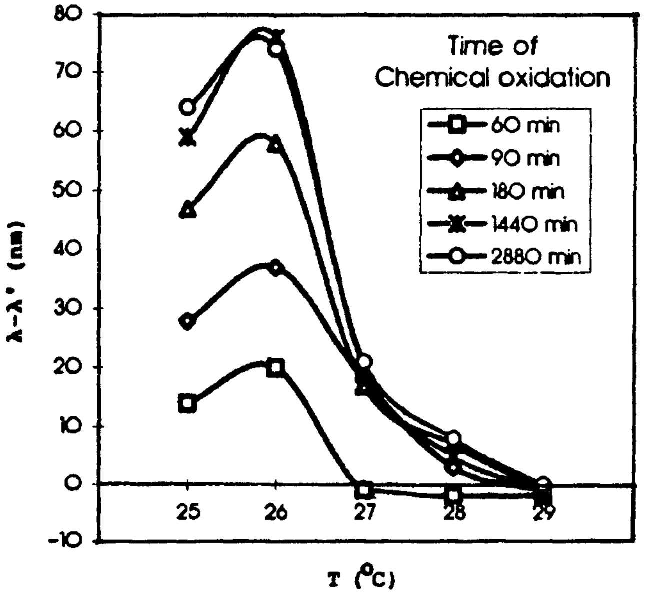

FIGURE 6 $\lambda - \lambda'$ vs temperature by different time intervals of chemical oxidation.

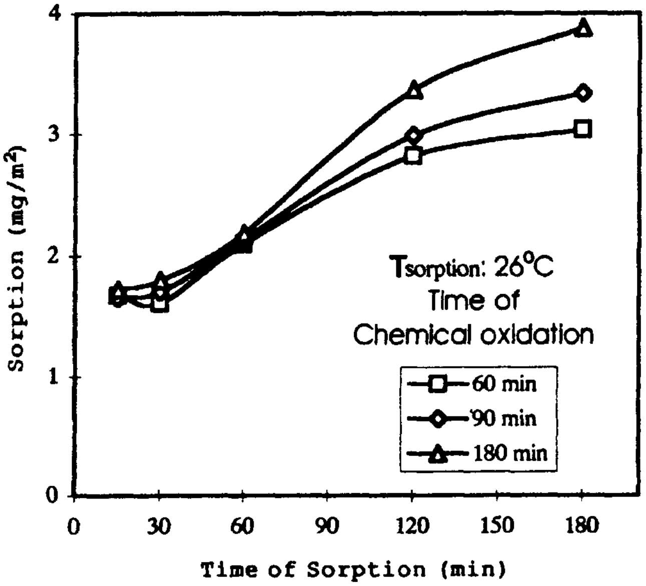

FIGURE 7 Sorption vs time by different time intervals of chemical oxidation.

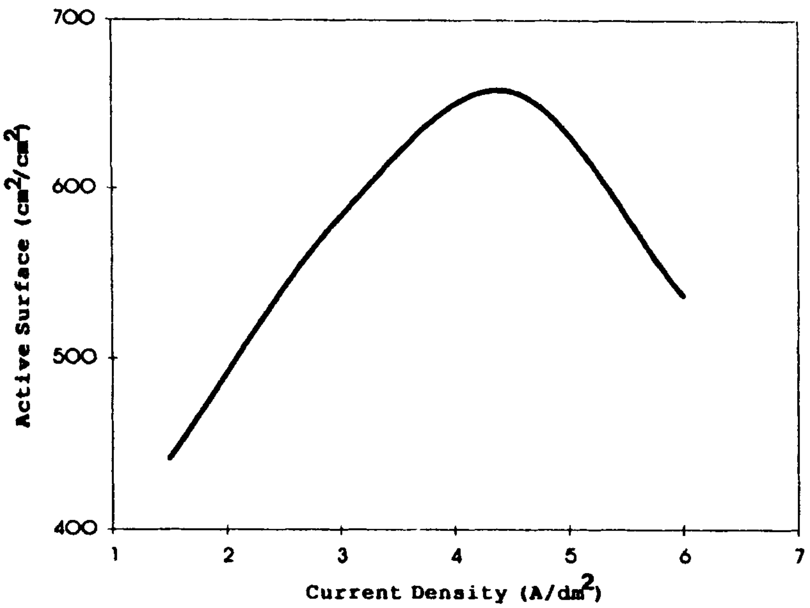

FIGURE 8 Active surface vs oxidation current density.

1.5 A/dm^2 increases up to 4.5 A/dm^2 and then decreases for 6 A/dm^2. This can be interpreted by the fact that by increasing the c.d. the size of the ZnO crystals decreases, the active surface increases, and the sorptive properties increase. After a certain c.d. the smaller crystals are anodically dissolved, the real surface decreases as well as the sorptive properties and the reflected wavelength decrease [18] (Fig. 8): The active surface was measured by the B.E.T method.

In paragraph 3.2.1.1 (Fig. 4), we saw that the influence of the oxidation time (current quantity) on the reflected wavelength by the Ch.L.C. spread on the specimens is high, contrary to the results on ZnO on pure Zn (measurements, 2.2.2). The last was attributed to the unappreciable change of the real surface by the increase of current quantity. In order to prove that under the conditions of Figure 4 the active surface changes with the current quantity, B.E.T. measurements were carried out (Fig. 9).

We see that indeed, increasing the time of oxidation, the active surface (cm^2/cm^2/: real/geometric) increases.

The difference in behaviour between electrolytically and chemically prepared ZnO on galvanized steel sheets (very higher shift for the electrolytic oxide: Figs. 4 and 6) is due to the different microstructure of the two types of oxides (electrolytically and chemically oxidized) (Figs. 10a, b) and to the doping of ZnO with Fe_xO_y during electrolytic oxidation. This can be seen in XR Electron Probe Microanalysis (EPMA) diagrams (Fig. 11). (E.D.S).

We see the increase from *a* to *c* of the iron concentration on the surface of ZnO due to the diffusion of Fe^{2+} from steel vs time of anodizing.

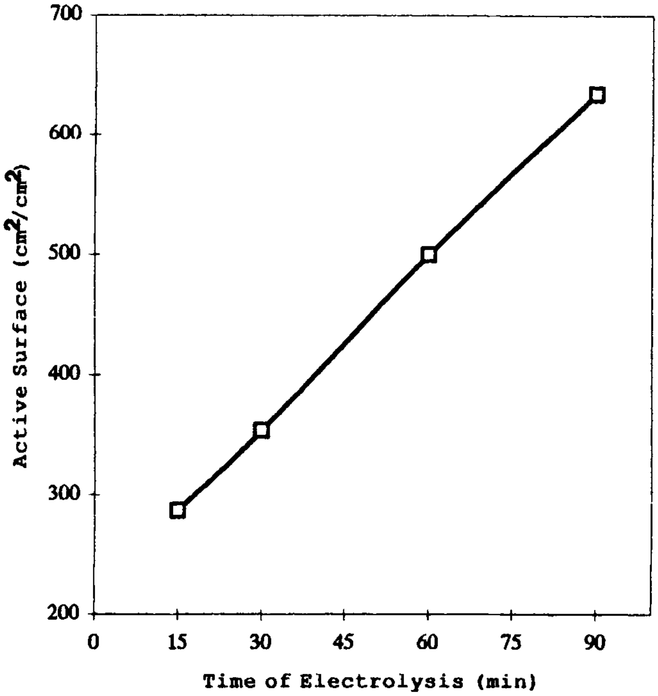

FIGURE 9 Active surface vs time of electrolysis.

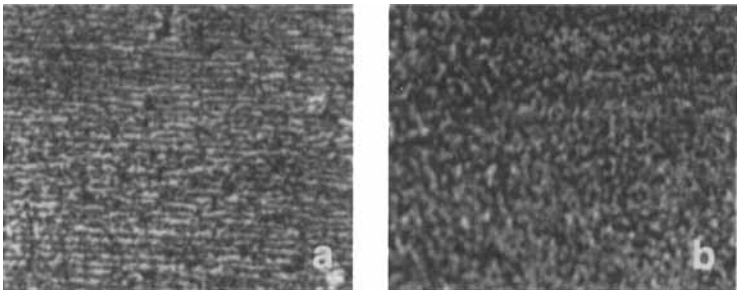

FIGURE 10 Surface of galvanized steel sheet: (a) chemically oxidized; (b): electrolytically oxidized X100.

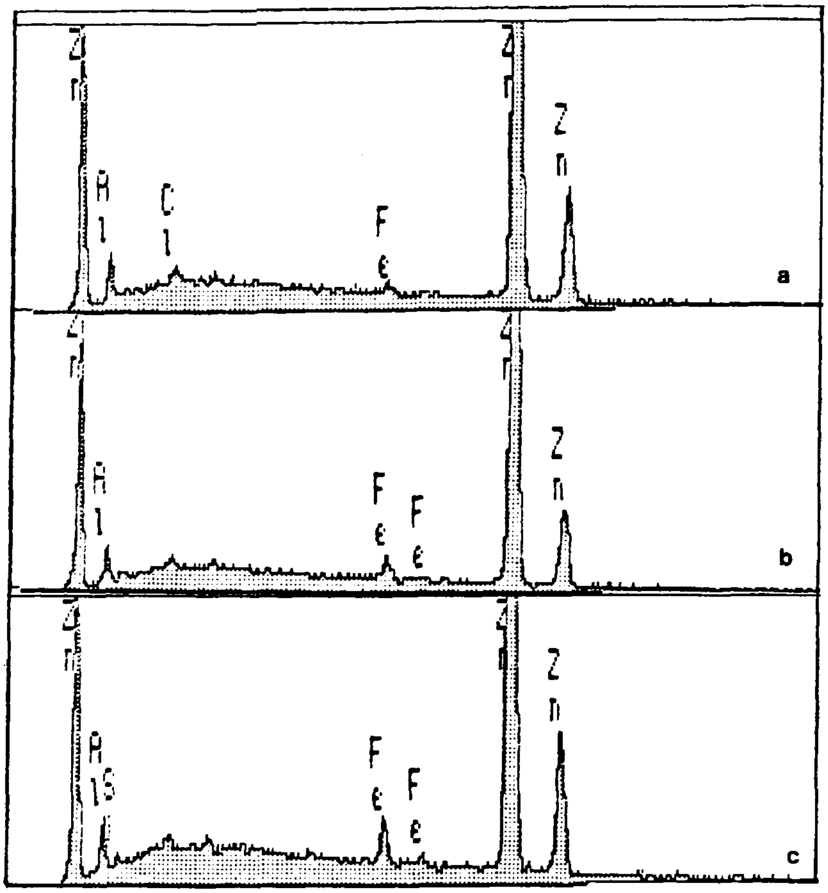

FIGURE 11 E.D.S. (Electron Dispersive Spectrometry). Iron concentration on the surface of ZnO of galvanized steel sheets vs time of anodizing. From *a* to *c* the time of anodizing increases as well as the concentration of iron due to the diffusion of Fe^{2+} during anodizing.

If we correlate the diagrams of Figure 4 with those of Figure 5 and of Figure 6 with those of Figure 7, the diagrams of Figures 12, 13, 14, (for electrolytically oxidized specimens of galvanized steel) and of Figures 15, 16, 17 (for chemically oxidized specimens of galvanized steel) are valid.

We see in all cases the rectilinear function $(\lambda - \lambda')_T = as' + b$ between $\lambda - \lambda'$ (shift at the peak of the wavelength of diffusion reflectance spectroscopy: λ on the specimens and λ' on blackened glass) and s' (sorption expressed in mg/m^2 methylene blue).

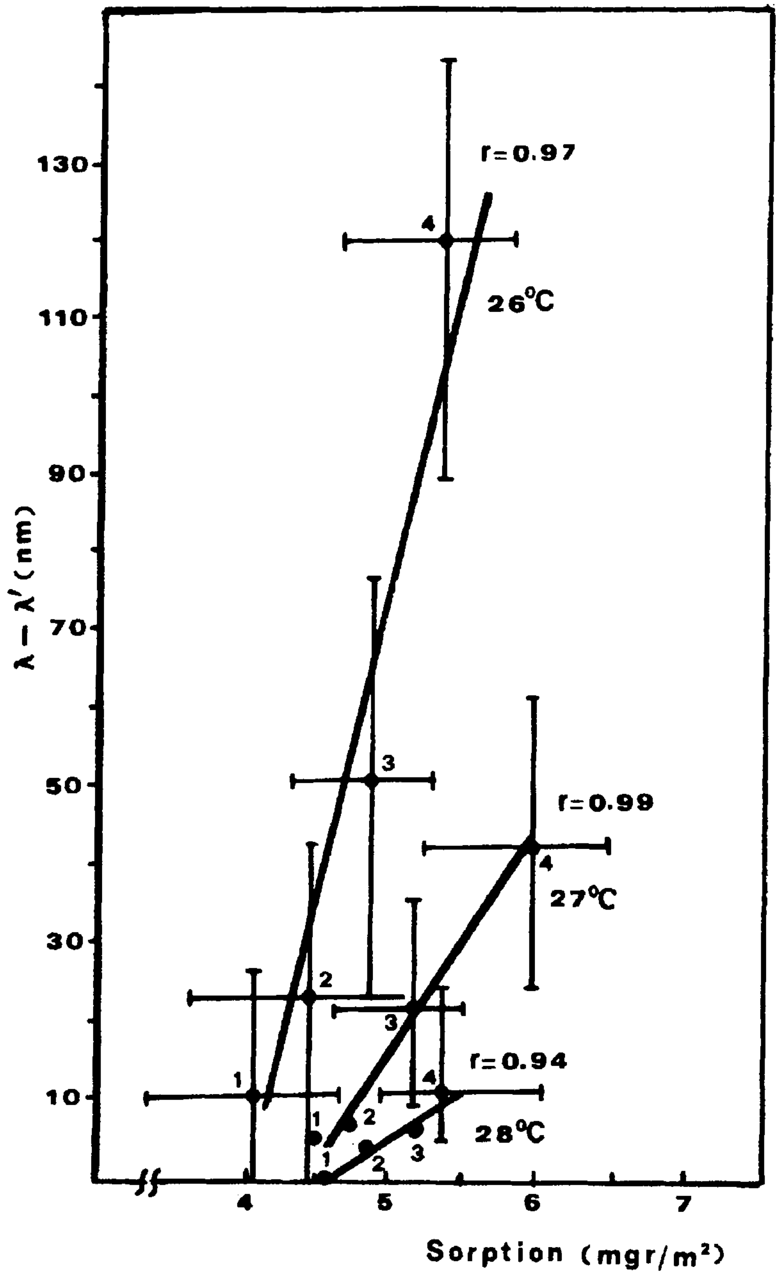

FIGURE 12 Diagram $\lambda - \lambda'$ vs sorption for three temperatures. Each pair of $\lambda - \lambda'$ and s' was measured, at the same temperature. 1, 2, 3, 4 are the mean of the value fluctuations in the cross area for different times of anodizing: 15, 30, 60, 90 min. Time of sorption 60 min.

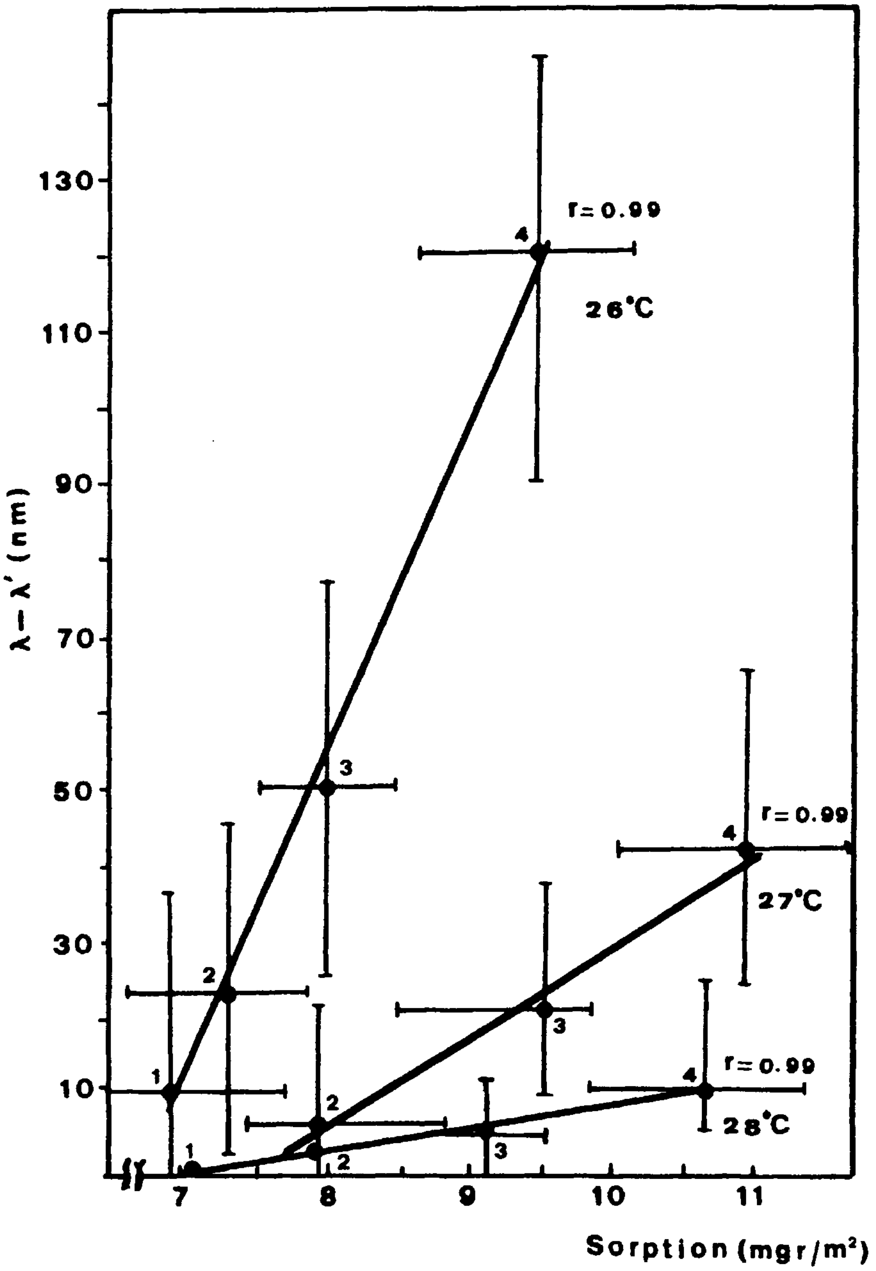

FIGURE 13 As 12. The difference is only on the time of sorption: 90 min instead of 60 min.

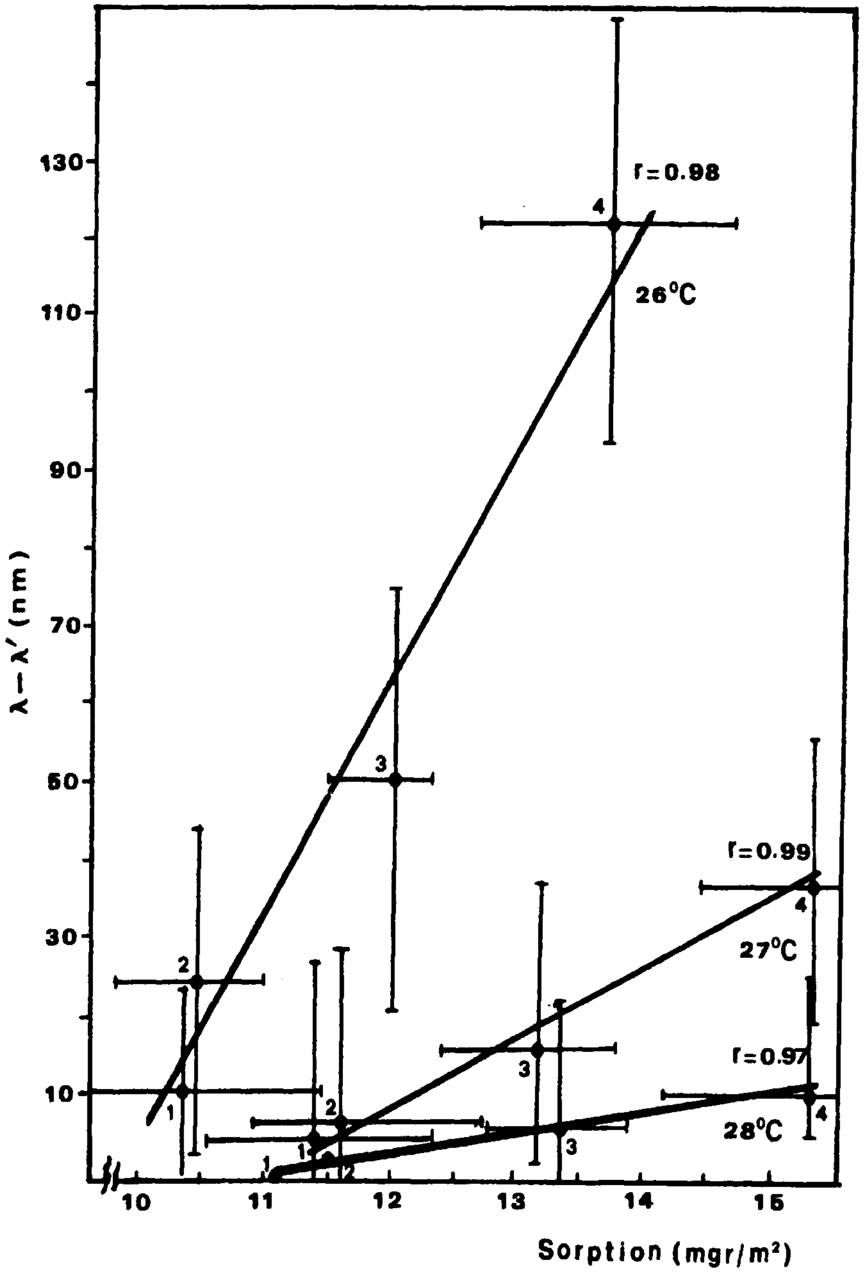

FIGURE 14 As 12. The difference is only on the time of sorption: 180 min instead of 60 min.

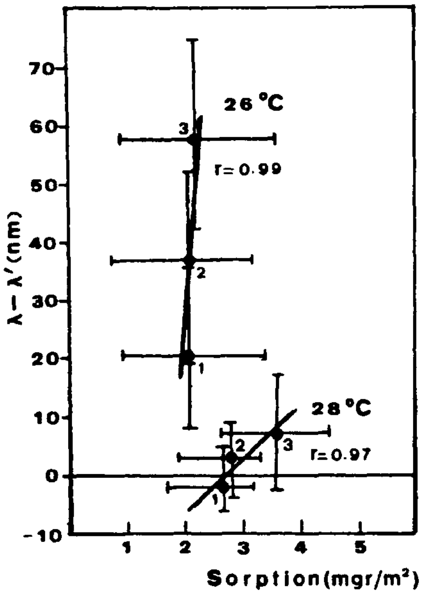

FIGURE 15 Diagram $\lambda - \lambda'$ vs sorption, for two temperatures (26 and 28°C). Each pair of $\lambda - \lambda'$ and s' was measured at the same temperature. 1, 2, 3 are the mean of the value fluctuation in the cross area for different times of chemical oxidation: 60, 90, 180. Time of sorption 60 min.

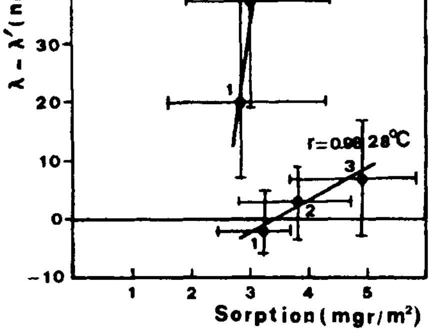

FIGURE 16 The same as 15. The difference is only on the time of sorption: 120 min instead of 60 min.

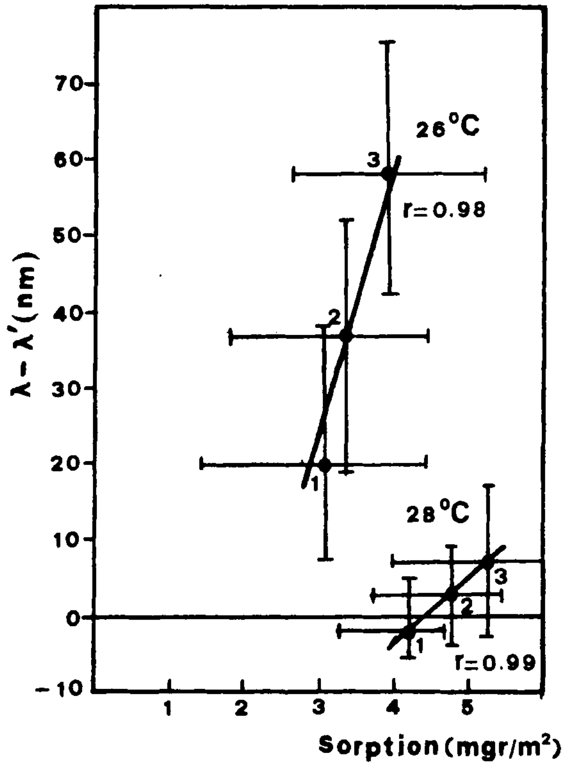

FIGURE 17 The same as 15. The difference is only on the time of sorption: 180 min instead of 60 min.

CONCLUSION

From the above mentioned it follows:

1. The findings of the previous work that the wavelength reflected by the cholesteric liquid crystals is also influenced by the sorptive properties of their supports is further proved, as well as that the quantity $\lambda - \lambda'$ is more sensitive than the λ.
2. The wavelength is also influenced by the ageing of the oxides, i.e. by their real active surface and consequently again by their sorptive abilities.
3. The ZnO prepared electrolytically on pure Zn shows an unappreciable difference in the influence on the reflected wavelength, if they are prepared by different current densities and current quantities. On the contrary, the ZnO prepared electrolytically on galvanized Fe-sheet, because they have

very different sorptive abilities vs current quantity, they also have different shifts.

4. For the wavelength the unequality is valid:

$$\lambda_{\text{uncoated}} < \lambda_{\text{ZnO chem.}} < \lambda_{\text{ZnO electr.}}$$

5. During electrolysis for galvanized Fe-sheets, the Fe^{2+} diffuses through the Zn film and its oxides dope the ZnO.
6. The equation of the previous work between $\lambda - \lambda'$ and sorption: $(\lambda - \lambda)_T = as' + b$ is also qualitatively valid for the electrolytically and chemically prepared ZnO on galvanized steel sheets by different current quantities.

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