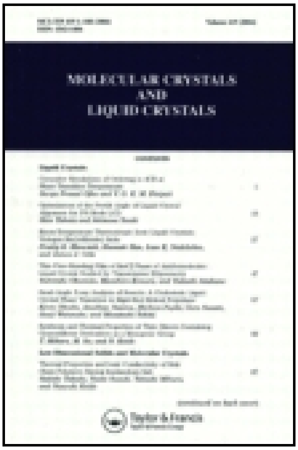

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Influence of Solid Support Sorptive Properties on the Color of Cholesteric Liquid Crystals

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Influence of Solid Support Sorptive Properties on the Color of Cholesteric Liquid Crystals

II. Quantitative Results

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This work is a continuation of that published in Part I [*Mol. Cryst. Liq. Cryst.*, **61**, 31 (1980)] under the same title, where the qualitative influence of the solid support sorptive properties on the reflected wavelengths from cholesteric liquid crystals has been for the first time reported. It was visually observed that the reflected light band shifted to longer wavelengths as the sorptive abilities of the solid support increased.

In the present work, quantitative measurements (visible diffuse reflectance spectroscopy) at several temperatures on bare metal (Zn, Fe, Cu, Al) surfaces mechanically treated, on chemically and electrolytically prepared ZnO and Fe_3O_4, on electrolytically prepared γ_1– and γ_2–Al_2O_3, on copper surfaces electroplated with copper and on electrolytically prepared γ_1–Al_2O_3 under several current densities, covered with the same mixture of cholesterics as the one used in the previous work, were carried out. Thus, the results of the visual observations of the previous work were checked and the following relationship between the reflected wavelength at the peaks (λ) from the examined cholesteric system on γ_1–Al_2O_3 and on blackened glass (λ') and the physical sorptive abilities of the γ_1–Al_2O_3 (s') as a function of temperature [T(°K)] was temporarily established:

$$(\lambda - \lambda')_T = (-0.1T + 30.28)s' + \left[-121.3\,\frac{10^6}{T^2} + 1351\right]$$

INTRODUCTION

In a previous work of ours[1] the influence of the sorptive properties of the solid supports on the reflected visible light band (color) of the cholesteric liquid crystals was for the first time observed and reported. The interpretation given was that the solid sorbents act on the sorbates with strong mechanical or/and electrical forces and consequently they have the same influence on the cholesteric liquid crystals as the pressure[2–5] or the electric field.[6–9] As solid supports the same chemically and electrolytically prepared metal oxides on metal surfaces (ZnO, Fe_3O_4), with different secondary structure (γ_1–Al_2O_3, γ_2–Al_2O_3), with several thicknesses (γ_1–Al_2O_3) or prepared under different current densities (γ_1–Al_2O_3), as well as surfaces of the same metal (Cu) mechanically treated and electroplated by the same metal (Cu) were used. In all cases a qualitative differentiation of the known[10,11] sorptive properties between the compared solid supports could be proved, based on the shifting of the reflected light band. The rule that the reflected light band is usually shifted to longer wavelengths as the temperature decreases was also observed for all supports and for the cholesteric mixture used. These observations could have resulted in an extension of the application for visible reflection of cholesterics reflecting UV light at a temperature region, and to the following possible applications realizing quantitative measurements: collecting data on the structure of the cholesteric mesophase, prediction of the chemical, the catalytical, the sorptive activity of a solid and the corrosion tendency of an alloy, checking the effectiveness of sand blasting, etc.

All the above mentioned experiments and results were based on visual observations and the results were only qualitative.

In the present work, quantitative measurements at several temperatures, using visible diffuse reflectance spectroscopy, were carried out on bare metal surfaces (Zn, Fe, Cu, Al) mechanically treated, on chemically and electrolytically prepared ZnO and Fe_3O_4, on electrolytically prepared γ_1- and γ_2-Al_2O_3,[12–14] on copper surfaces electroplated with copper and on electrolytically prepared γ_1–Al_2O_3 under several current densities, since from previous works of ours their secondary structure[15] and all their sorptive (chemical[12,13] and physical),[11] catalytic,[16] aging,[17,18] protective (related to sorption)[19] against stress corrosion cracking[19–22] properties were known. Part of this work was presented in an international seminar.[23]

EXPERIMENTAL

Materials, shape, dimensions and preparation of the specimens

The materials [metal sheets 0.5 mm thick Zinc 99.9% + (Fe, As) 0.1%, Steel 99.28% + C 0.12% + Mn 0.5% + S 0.05% + P 0.05%, Copper 98% + (As + Fe + P) 2%, Aluminum 99.7% + (Si + Fe + Ti + Cu + Zn + traces of other elements) 0.3%], the cholesteric mixture [1 : 4

cholesteryl-4-carbomethoxy-oxybenzoate and cholesteryloleylcarbonate 10% solution in diethylether] and the methods of anodizing for the preparation of ZnO, Fe_3O_4, $\gamma_1-Al_2O_3$ and $\gamma_2-Al_2O_3$ on metal sheets surface, of chemical oxidation of Zn and Fe sheet surfaces and of electroplating Cu were the same as in the previous work;[1] the shape and the dimensions of the specimens to be anodized or chemically oxidized were: 5 × 9.5 cm and of the specimens to be measured 2.5 × 3 cm.

Experiments, experimental procedure and results

On all types of specimens visible diffuse reflectance spectra at several temperatures were taken before and after covering the surface with the above mentioned cholesteric mixture, as well as on blackened glass (sorption almost inactive).

Precisely the cholesteric mixture (always 0.8 ml) was spread over the surface of the specimens by the aid of a syringe in order to assure the same thickness of the cholesteric mixture ($50 \div 60$ μm) for all cases after the evaporation of the diethylether. The complete evaporation of the diethyl ether was assured by heating the specimens (placed horizontally on a thermostated surface) over the isotrotic transition point. Then the specimen was allowed to cool and by a cover-slip displacement on the surface of the specimen the Grandjean texture was imposed to the cholesterics. For the measurements, a Perkin-Elmer double beam spectrophotometer (mod. 124) for visible light with an integrating sphere attachment (124-0049 Hitachi) was used. Each specimen with the cholesteric mixture, treated as mentioned above, was placed on a special thermostated block-heater in the apparatus (in the place designated for back reflection measurements) and was normal to the light beam. In this way the spectra were taken at a desirable constant temperature ±0.1°C. The accuracy of the measurements was ±0.5 nm.

For accuracy and reproducibility reasons many spectra were taken on the same specimen, on specimens cut at different sites of the same treated sheet and on specimens of the same type prepared separately under the same conditions.

For all cases the wavelength at the peak of the spectra was determined. The difference $(\lambda - \lambda')$ of wavelengths at the peaks for the specimens (λ) and blackened glass (λ') was found to be the most sensitive measure of the shift of the peaks. The dispersion of these values fluctuated ±4% for the measurements on blackened glass and on bare metals and ±8% for those on treated surfaces due to their unhomogeneity.

The corresponding values for the sorptive abilities of the solid supports (mg of methylene blue sorbed per m^2 from 1% solution up to 23 h) were taken from a previous work of ours.[11]

I. Measurements at several temperatures on blackened glass (background) and on bare steel, zinc, copper and aluminum specimens mechanically cleaned Using the above mentioned technique the following spectra for steel covered with the cholesteric mixture at several temperatures resulted (Figure 1). In Table I the values at the peaks at several temperatures for steel, covered with the cholesteric mixture, are shown to demonstrate the repeatability of the measurements.

In Table II the mean of wavelengths at the peaks at several temperatures for the four metals used and for blackened glass, covered by the cholesteric mixture, as well as the values of $\lambda - \lambda'$ are presented.

From Table II follows the diagram (Figure 2).

II. Comparison between chemically (c.p.) and electrolytically prepared (e.p.) ZnO and Fe_3O_4; copper mechanically treated and electroplated with copper; γ_1–Al_2O_3 *and* γ_2–Al_2O_3 The results on chemically and electrolytically prepared ZnO and Fe_3O_4, on copper surface mechanically treated and electroplated with copper, as well as on γ_1– and γ_2–Al_2O_3 (3A/dm^2, thickness 8 μm for both oxides, 27°C), are shown in Figures 3 and 4.

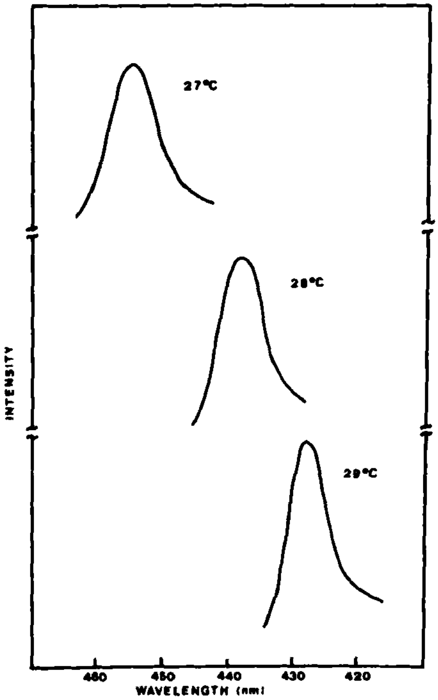

FIGURE 1 Spectra at several temperatures of steel covered with the cholesteric mixture.

TABLE I

Wavelengths at the peaks at several temperatures for steel specimens, covered with the cholesteric mixture

	Temperature (°C)		
	27	28	29
Wavelengths (nm)	443	423	413
	467	447	435
	470	450	438
	455	438	428
	430	416	413
	428	418	415
Mean	449	432	424
SD	±18	±15	±12

TABLE II

Mean (8 measurements) of wavelength values at the peaks (λ) at several temperatures for steel, Al, Zn and Cu, for blackened glass (λ') and the values of $\lambda - \lambda'$

		Wavelengths (nm)				$\lambda - \lambda'$			
Temperature (°C)	Blackened glass (λ')	Steel (λ_S)	Al (λ_{Al})	Zn (λ_{Zn})	Cu (λ_{Cu})	Steel	Al	Zn	Cu
26	451	—	—	—	—	—	—	—	—
27	423	449	441	438	433	26	18	15	10
28	411	432	428	421	420	21	17	10	9
29	406	424	424	416	414	18	18	10	8

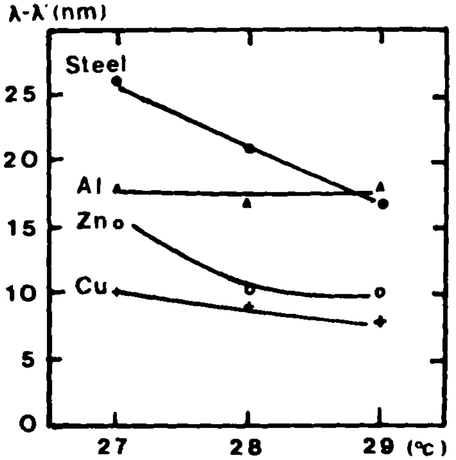

FIGURE 2 $\lambda - \lambda'$ for Steel (●), Al (▲), Zn (○), and Cu (+) at several temperatures.

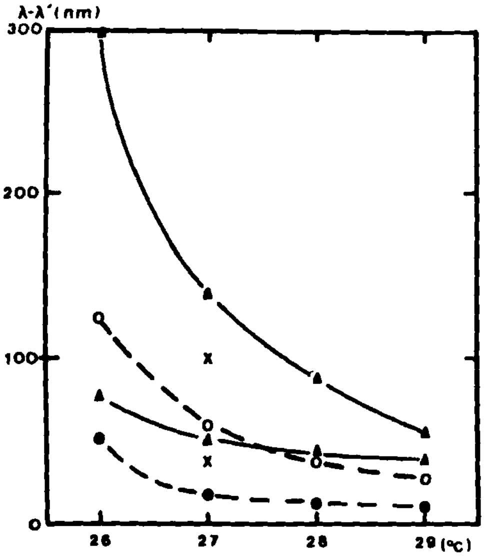

FIGURE 3 Comparison by $\lambda - \lambda'$ between chemically (●) and electrolytically (○) prepared ZnO, chemically (▲) and electrolytically (△) prepared Fe_3O_4 and γ_1–Al_2O_3 (x), γ_2–Al_2O_3 (x').

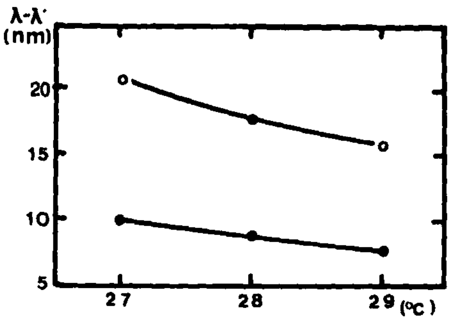

FIGURE 4 Comparison by $\lambda - \lambda'$ between Cu mechanically treated (●) and electroplated with Cu (○).

III. Measurements at several temperatures on γ_1–Al_2O_3 prepared under several current densities for the same thickness (18.8 μm) In Figure 5 the spectra of γ_1–Al_2O_3, prepared under several current densities, covered with the cholesteric mixture are presented.

In Figure 6 the mean values of the sorption for 18.8 thick γ_1–Al_2O_3 and of $\lambda - \lambda'$ (8 measurements) on γ_1–Al_2O_3 of the same thickness at several temperatures vs preparation current densities (1.5, 3, 4.5, 6 A/dm^2) are presented.

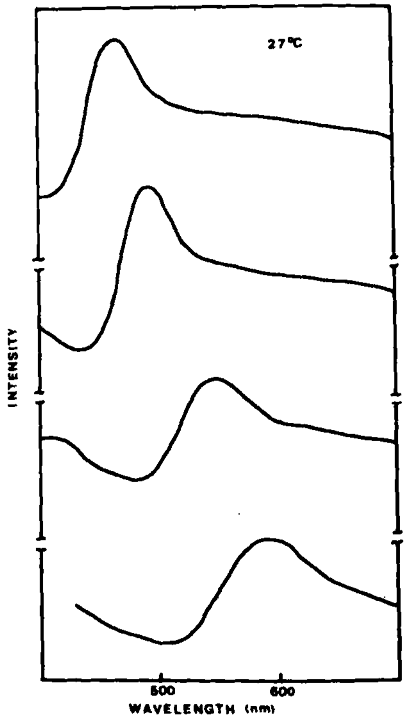

FIGURE 5 Spectra at 27°C of γ_1–Al_2O_3, prepared under several current densities (decreasing downwards: 6, 4.5, 3, 1.5A/dm^2), covered with the cholesteric mixture.

From the diagram of Figure 6 the diagram of Figure 7 is aquired, where $\lambda - \lambda'$ vs sorption is shown.

DISCUSSION

From the above mentioned experiments and results, it follows the general conclusion that indeed the sorptive properties of the support of the mixture of the cholesteric liquid crystals influence their reflected band of visible light.[1] Furthermore, from the quantitative measurements we can now also draw quantitive conclusions, based on objective results (wavelength value at the peak) and not, as in Part I on subjective visual observations:

i.1. From the results of the first series of experiments on bare metals (Figure 2) the following inequalities are valid for all three examined temperatures (with the slight exception between Steel and Al at 29°C):

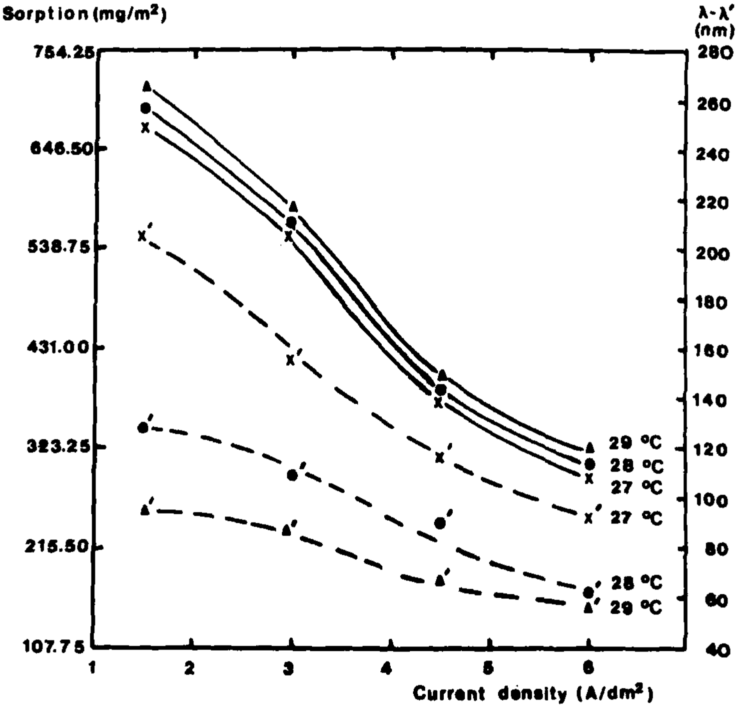

FIGURE 6 Sorption and $\lambda - \lambda'$ vs current density at several temperatures; sorption: x, ●, ▲, $\lambda - \lambda'$: x', ●′, ▲′.

$$\lambda_{Fe} > \lambda_{Al} > \lambda_{Zn} > \lambda_{Cu}$$

and $$(\lambda - \lambda')_{Fe} > (\lambda - \lambda')_{Al} > (\lambda - \lambda')_{Zn} > (\lambda - \lambda')_{Cu}$$

Probably the same series can be valid for the sorption on their surface of methylene blue. Measurement of physical sorption on these metals has not been possible to take because of the extremely small sorbed quantities.

2. This shows once more[1] the sensitivity of the method to predict sorption abilities of surfaces using liquid crystals.

3. Theoretically these series can be justified by the fact that these metals follow the same series when acting as catalyst by sorption.[10,16,24-26] Another additional explanation is to take into account the corrosion tendency[1] from copper to aluminum, related also with their sorptive abilities, due to the formation of oxides on their active centers, having more intense sorptive abilities as the metal (Figures 2, 3). Thus, if we exclude the inequality of steel from Cu to Al it follows the place of the metals in the electromotive series, according to the rule higher rate of formation, higher sorptive activities. One explanation for the results on steel is that its

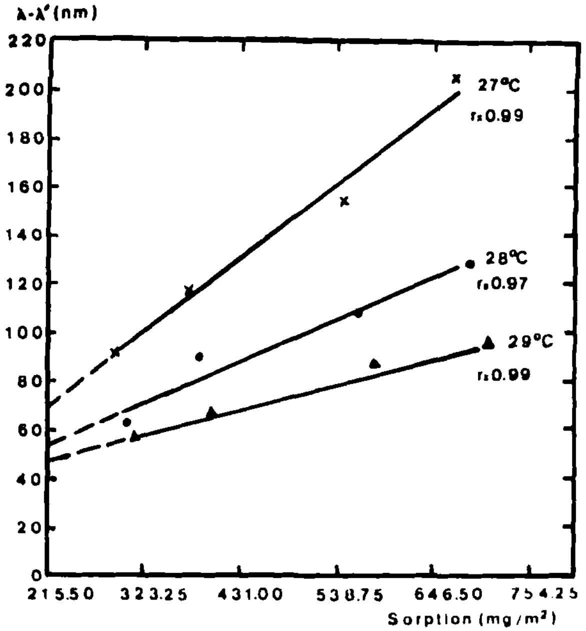

FIGURE 7 $\lambda - \lambda'$ vs sorption.

oxides formed on the active centers of its surface are more active than those of Al and Zn, because the latter are already aged due to the immediate formation of oxides after contacting the atmosphere. This is supported from the results of Figure 3.

4. In all cases increasing the temperature the reflected wavelength decreases (see Section iv of discussion).

ii.1. The results of the second series of experiments (Figures 3, 4) support the qualitative observations of Part I:

$$(\lambda - \lambda')_{\mathrm{Chem.Fe_3O_4}} > (\lambda - \lambda')_{\mathrm{el.Fe_3O_4}}$$

according to their known[12-24] sorptive and catalytic (by sorption) properties.[1] The same is true for $(\lambda - \lambda')_{\mathrm{e.p.ZnO}} > (\lambda - \lambda')_{\mathrm{c.p.ZnO}}$ for $(\lambda - \lambda')_{\mathrm{e.p.Cu}} > (\lambda - \lambda')_{\mathrm{mec.Cu}}$ and for $(\lambda - \lambda')_{\gamma_2\text{-}\mathrm{Al_2O_3}} > (\lambda - \lambda')_{\gamma_1\text{-}\mathrm{Al_2O_3}}$ According to their sorptive and catalytic (by sorption) properties.[10,16,23-27]

2. The differences are more pronounced as the temperature gets lower (see Figures 3 and 4). In all cases increasing the temperature the reflected wavelength decreases (see Section iv of discussion).

3. Concerning the γ_1- and $\gamma_2-Al_2O_3$ the following is valid: The mean value of $\lambda - \lambda'$ for $\gamma_1-Al_2O_3$ and for $\gamma_2-Al_2O_3$ for the same thickness ($\sim$8 μm), temperature (27°C) and current density of their preparation (3A/dm^2) is 41 and 102 nm respectively (Figure 3). The sorption[11] (1% methylene blue, 23 h) under the same conditions of preparation and at 27°C is 440 and 1191 mg/m^2 respectively. From these data the following equations are valid:

$$\frac{(\lambda - \lambda')_{\gamma_2-Al_2O_3}}{(\lambda - \lambda')_{\gamma_1-Al_2O_3}} \approx 2.5; \qquad \frac{s'_{\gamma_2-Al_2O_3}}{s'_{\gamma_1-Al_2O_3}} \approx 2.7$$

(where s': sorption: mg methylen blue per m^2).

We could suppose that in the frame of the experimental errors we have an almost satisfactory coincidence of the ratios, although the $\gamma_2-Al_2O_3$ spectra are flattened and therefore the peak is not as sharp as for $\gamma_1-Al_2O_3$ for an accurate determination. Thus temporarily between $\lambda - \lambda'$ and s' the following equation could be valid:

$$\lambda - \lambda' = a's'$$

(see Section iii.4 of Discussion).

iii. From the results of the third series of experiments it follows:

1. The form of the curves for sorption and for $\lambda - \lambda'$ is almost similar (Figure 6).

2. Increasing the current density of the preparation of the $\gamma_1-Al_2O_3$ the difference of the wavelengths $\lambda - \lambda'$ shifted to smaller values; the same is true for the physical sorptive abilities.[11]

3. The sorption abilities increase by increasing the temperature, as it is usually the case for sorption. Increase of the rate with the temperature; it is not a steady state equilibrium, where the amount of the physically sorbed substances decrease with a temperature increase. In addition to this, the coagulation of such a lyophobe molecular colloid as methylene blue is irreversible.

4. The determining factor for the shift is the physical sorptive abilities and not the chemical ones (as one could conclude and we make in the first part, based also on the no accurate visual observations, since even on physical sorption cases the first monolayers of the sorbates are considered to be chemically sorbed). That means that the influence (pressure or electrical field) of the sorbent-support is not limited to the first monolayers of the sorbates in the interface but is extended inside the film to the whole

adherent layer. It must also be noticed that the chemical sorption increases with the current density of the preparation of the oxide,[12,13] and that the catalytic properties (by electron exchange) is not related with the shift.

From Figure 7 we have the first quantitative relation between $\lambda - \lambda'$ shift and sorptive properties of the support.

From the same Figure it follows that the $\lambda - \lambda'$ shift of the reflected wavelengths is linearly proportional to the sorptive abilities of the solid support of the cholesteric mixture. In spite of the dispersion of the values of sorption and of wavelengths due to the experimental errors, the values fit well to a rectilinear equation, at different temperature, with correlation factors (least squares method) of 0.99 (27°C), 0.97(28°C), 0.99 (29°C). The equation is:

$$\lambda - \lambda' = a \cdot s' + c$$

where s': sorption and a,c: factors to be determined.

(a) Determination of a factor (slopes)

By using the least squares method the following values for the slopes a of the rectilinear relations were calculated for the three temperatures employed: 0.29 (27°C), 0.16 (28°C), 0.097 (29°C). Using these values the diagram of Figure 8 is drawn.

We observe a linear relation between the slope a and the absolute temperature:

$$a = -0.1T + 30.28$$

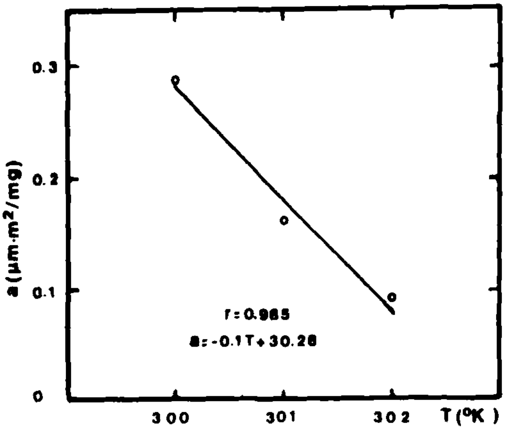

FIGURE 8 Slopes (Figure 7) vs absolute temperature.

with a correlation factor of 0.985.

The dimensions of a are: $[a] = [\text{nm}][\text{mg}]^{-1}[\text{m}]^2$.

(b) Calculation of the *c* factor (intercepts)

The following diagram (Figure 9) of c against $(1/T)^2$ was drawn.

Between c and $(1/T)^2$ the following equation (least squares method) is valid:

$$c = -121.3\left(\frac{10^3}{T}\right)^2 + 1351$$

with a correlation factor of 0.98.

The dimensions of c are: $[c] = [\text{nm}]$.

(c) Quantitative relationship between reflected wavelength and sorption

Combining the equations of Figure 7 and those of (a) and (b) we found:

$$(\lambda - \lambda')_T = (-0.1T + 30.28)s' + \left[-121.3\frac{10^6}{T^2} + 1351\right]$$

where λ: the mean of the wavelengths at the peaks of visible diffuse reflectance spectra at a temperature T for the used cholesteric mixture when covering $\gamma_1\text{–Al}_2\text{O}_3$ 18.8 μm thick, prepared under several current densities, λ': the mean of the wavelengths at the peaks of visible diffuse reflectance spectra for the same cholesteric mixture at the same temperature T,

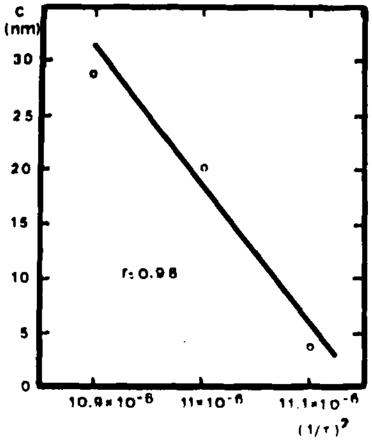

FIGURE 9 Intercepts (Figure 7) vs $(1/T)^2$.

when covering blackened glass, *s'*; sorption of methylene blue (mg/m^2, from 1% solution, and dyeing time 23 h) for the same γ_1–Al_2O_3 thickness (18.8 μm) at the same temperatures (27 ÷ 29°C) and prepared at the same current densities.

(d) Checking of the equation

In the following table (Table III) a comparison of the $\lambda - \lambda'$ measured values, to the $\lambda - \lambda'$ ones calculated by the above mentioned equation, is made.

Taking also into account the above mentioned experimental error ±8%, it follows to a quite satisfactory coincidence between the measured and calculated values of $\lambda - \lambda'$.

Another data, that supports the validity of the equation, is to calculate the ratio:

$$\frac{(\lambda - \lambda')_{\gamma_2\text{-}Al_2O_3}}{(\lambda - \lambda')_{\gamma_1\text{-}Al_2O_3}} = 2.5 \quad \text{at } 27°\text{C}$$

(see Section ii.3 of the discussion) by the aid of the established equation:

$$\frac{(\lambda - \lambda')_{\gamma_2\text{-}Al_2O_3}}{(\lambda - \lambda')_{\gamma_1\text{-}Al_2O_3}} = \frac{(-0.1 \times 300 + 30.28)1191 - 121.3\dfrac{10^6}{(300)^2} + 1351}{(-0.1 \times 300 + 30.28)440 - 121.3\dfrac{10^6}{(300)^2} + 1351}$$

$$= 2.66$$

TABLE III

Comparison of $\lambda - \lambda'$ measured and calculated by measn of the equation for γ_1–Al_2O_3 18.8 μm thick prepared under several current densities and temperatures

T (°K)	Current density (A/dm^2)	Sorption mg/m^2	($\lambda - \lambda'$) meas. (nm)	($\lambda - \lambda'$) cal. (nm)	% Mean difference
300	6	299.98	92.50	87.24	±8
	4.5	374.97	117.03	108.29	
	3	549.96	155.73	157.28	
	1.5	668.74	205.86	190.24	
301	6	308.98	62.40	67.80	
	4.5	386.22	91.65	81.71	
	3	566.46	109.98	113.16	
	1.5	688.80	129.44	146.18	
302	6	318.25	58.20	46.98	
	4.5	397.81	66.98	53.34	
	3	583.45	88.24	68.19	
	1.5	709.46	95.18	78.57	

i.e. there is a coincidence between the measured ratio and the calculated with an error of 6.4%. In spite of these agreements the validity of the equation is limited to the cholesteric mixture used, the proportions of its two components and the conditions employed, until it is proved to have a more general validity.

iv. By comparing the measured values of λ at several temperatures to the values that follow from the two equations of the literature[2,6–8] relating λ with T:

$$\lambda_T = \frac{A}{T}\left(1 + \frac{B}{T - T_0}\right)^2 \quad \text{and} \quad \lambda_T = \lambda_0 + \frac{B'}{(T - T_0)^2}$$

(where A, B, B', T_0, λ_0 are coefficients, that were determined by solving the systems using the couples of values λ_T (measured) $-$ T), it was found that both equations are valid with the same approximation.

CONCLUSIONS

From the present work it resulted:

1. The influencing factor of the support on the wavelength shift of the reflected light band from the cholesteric mixture used[1] is the physical sorption properties of the support or its catalytic ones by sorption and not the chemical ones or the catalytic by electron exchange.

2. For the present the most suitable measure for the comparison between the sorptive properties of the solid supports and the wavelength shift is $\lambda - \lambda'$ (where λ and λ' the wavelengths at the peaks when the cholesteric mixture covers the solid support and a blackened glass correspondingly). The values of λ, λ' resulted from the corresponding visible diffuse reflectance spectra.

3. For all examined cases the $\lambda - \lambda'$ increases with the physical sorptive activity (s') of the supports.

4. Measurements on bare metal surfaces (Zn, Al, Cu, Fe) revealed quantitatively the difference of their physical sorptive properties (sorption of methylene blue), which is impossible to have it measured directly due to the very small amount sorbed.

5. Quantitative relationships, revealing the difference on sorptive properties between chemically and electrolytically prepared metal oxides (ZnO, Fe_3O_4, Al_2O_3), as well as between the same oxides with different secondary structure (γ_1–Al_2O_3, γ_2–Al_2O_3) and between different surfaces (mechanically treated and electroplated) of the same metal (Cu) can be established.

6. The following equation, relating $\lambda - \lambda'$ and the physical sorptive abilities (s') is valid: $\lambda - \lambda' = as' + c$. The following equation as a function of the absolute temperature (T) was established and checked:

$$(\lambda - \lambda')_T = (-0.1T + 30.28)s' + \left[-121.3\frac{10^6}{T^2} + 1351\right]$$

This equation is limited to the conditions of the experiments (i.e. γ_1–Al_2O_3, 18.8 μm thick, prepared under current densities between 1.5 and 6 A/dm^2, the cholesteric mixture used and at 26 ÷ 29°C) and therefore can be extended and improved with additional measurements; it is more accurate at low temperatures.

7. When comparing substances, the difference $(\lambda_1 - \lambda') - (\lambda_2 - \lambda') = \lambda_1 - \lambda_2$ increases lowering the temperature.

Acknowledgments

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