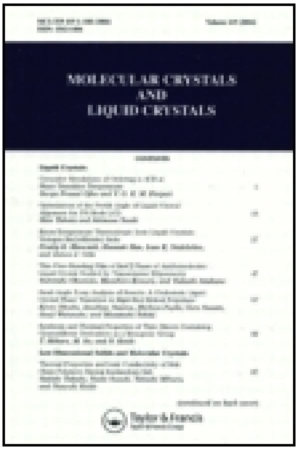

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Influence of Solid Support Sorptive Properties on the Color of Cholesteric Liquid Crystals
I. Qualitative Observations

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The influence of solid support sorptive properties on the color of cholesteric liquid crystals is for the first time reported. The reflected light band shifts to longer wavelengths as the sorptive abilities increase. Differentiation of sorptive intensities between the same chemically and electrolytically prepared oxides on metal surfaces, with different secondary structure ($\gamma_1 - Al_2O_3$, $\gamma_2 - Al_2O_3$), with different thicknesses or prepared with different current densities, and between two metal surfaces, one mechanically cleaned and the other electroplated with the same metal, is possible. Thus: (a) An extension of the applications for visible reflection of cholesterics, reflecting U.V. light at a certain temperature region, can be realized; (b) Data about the structure of the cholesteric mesophase can be perhaps revealed; (c) New laboratory methods of measuring the sorptive intensity and the chemical or catalytic activity of solids, the corrosion tendency of metals and the effectiveness of sand blasting can, besides others, be developed.

INTRODUCTION

As it is known, the reflected light band by the cholesteric liquid crystals is usually shifted to longer wavelengths as the temperature decreases[1-3] or the applied pressure increases;[4-7] electric[1-3,8] or magnetic[1-3,8,9] fields and small quantities of impurities[10] also change their color. This color change is the result of the influence of the above mentioned parameters upon the pitch.[1-10] The sensitivity of the color change is extremely strong in the neighborhood of a cholesteric-to-smectic phase transition.[2,7]

We thought that if we used solid sorbents as supports of cholesteric liquid crystals the selectively reflected light of the latter could also be influenced, since the sorbents act on the sorbates with big mechanical or/and electrical forces, such as the applied pressure[4-7] or the electric field[1-3,8] correspondingly. To check this idea, we used as supports of liquid crystals a number of known metal oxide sorbents, some of which were prepared in our laboratory and studied from their structure, sorption, catalytic and anticorrosive properties point of view;[11-25] we also used active metal surfaces.

EXPERIMENTAL

Materials, shape, dimensions and preparation of the specimens

In order to realise the above mentioned, flat and homogeneous surfaces as supports of the liquid crystals were needed for the experiments. For this reason oxides (Al_2O_3,Fe_3O_4,ZnO), prepared on metal surfaces chemically and electrolytically were used. It has been shown[11,12,17,23] that these two kinds of oxides have different sorptive properties. This was desirable since both kinds of oxides (prepared chemically and electrolytically) have the same chemical composition and color (except ZnO), facilitating the comparison and the interpretation of the results. On the other hand the electrolytic preparation leads to the formation of oxides of the same metal with different secondary structure and sorptive properties, but with the same color and chemical composition [e.g. γ_1-Al_2O_3, γ_2-Al_2O_3].[11,12,22,23,25] In addition to these, the electrolytic preparation of γ_1-Al_2O_3 provided oxide layers of several thicknesses and, under several current densities, resulting in oxide surfaces with different sorptive properties.[11,12,14,23] Bare metal surfaces mechanically cleaned and electroplated with the same metal, having a different number of active centers of different intensity, were also used. All four series are also adequate to reveal the sensitivity of the sorption influence of the supports on the color of cholesterics.

The specimens supports were prepared from aluminum, copper, nickel, zinc, and steel sheets of 0.5 mm thickness, their dimensions were 5 × 3 or 5 × 5 cm^2. The nominal composition in weight per cent of these metals was:

Aluminum: 0.3 Si, Fe, Ti, Cu, Zn and traces of other elements, remainder 99.7 Al; Copper: 2 As, Fe, P, remainder 98 Cu; Nickel; 0.1 Fe, remainder 99.9 Ni; Zinc: 0.1 Fe, As, remainder 99.9 Zn; Steel: 0.12 C, 0.5 Mn, 0.05 S, 0.05 P, remainder 99.28 Fe.

From these metal sheets the following kinds of specimens were prepared:

i Aluminum oxide specimens

a) Electrolytically-prepared γ_1-Al_2O_3. Aluminum specimens were electrolytically oxidized (by anodic oxidation) in a 15% H_2SO_4 solution with two lead electrodes as cathode and with a current density of 6 A/dm^2 at 25°C for 9 min.[11,12,14,22]

b) Electrolytically-prepared γ_2-Al_2O_3^{n} Aluminum specimens were electrolytically oxidized as in i.a. for 27.5 min.[11,12,14,22]

c) Electrolytically-prepared γ_1-Al_2O_3 *with the same current density* ($3A/dm^2$) *and several thicknesses:* Aluminum specimens were electrolytically oxidized separately with a current density of 3 A/dm^2 for 8.32, 16.64, 24.96, 33.38 min; thus γ_1-Al_2O_3 was prepared with thicknesses of 6.27, 12.54, 18.81, 25.08 μm.[14]

d) Electrolytically-prepared γ_1-Al_2O_3 *with several current densities and the same thickness:* Aluminum specimens were electrolytically oxidized separately as in i.a, with current densities of 1.5, 3, 4.5, 6 A/dm^2 for 33.3, 16.65, 11.1 and 8.32 min.

ii Zinc oxide specimens

a) Chemically-prepared ZnO: Zinc specimens were chemically oxidized by immersion in a 30% H_2O_2 solution, at 25°C, for 60 min.

b) Electrolytically-prepared ZnO: Zinc specimens were electrolytically oxidized in a 0.5 N NaOH bath, at 25°C, with a current density of 1.5 A/dm^2 for 60 min.[24]

iii Iron oxide specimens

a) Chemically-prepared Fe_3O_4*:* Steel specimens were chemically oxidized at 550°C for 3 hours and slowly cooled.[27]

b) Electrolytically-prepared Fe_3O_4*:* Steel specimens were electrolytically oxidized in a solution containing 120g NaOH, 10g $CH_2(OH)SO_2Na$ (Rhogalit) per L using two lead electrodes as cathode at 40°C with alternating current of 15A/dm^2 for 20 min.[28]

iv Copper specimens (bare surface)

a) Mechanically-cleaned surface: The surface of copper specimens was mechanically cleaned with emery paper after immersion in hydrochloric acid.

b) Electroplated surface: On the surface of copper specimens, treated as in iv, a, a copper film was deposited by electrolysis in a solution containing 150 g $CuSO_4 \cdot 5H_2O$, 50 g H_2SO_4 conc. and 50 g C_2H_5OH per L at 25°C with two copper electrodes as cathode and with a current density of 3 A/dm^2 for 5 min.

Occasionally several of those kinds of specimens (i.e., i.,a,b–ii.,a,b–iii.,a,b–iv.,a,b) were prepared on different places of the same metal sheets (10 × 3 cm^2) to compare them easily.

EXPERIMENTS, EXPERIMENTAL PROCEDURE AND OBSERVATIONS

a) All kinds of specimens were placed on a controlled constant temperature metallic surface and a commercial paper with encapsulated cholesteric liquid crystals (Firma EURAND) was placed on them. Pictures were taken at different temperatures: 24–27°C.

In the pictures (Figures 1, 2) all the film surface covering the different kinds of specimens (oxides or bare metals on the same metal sheet) has the same color, meaning that all the surface has the same temperature. It must be noticed that the sorptive abilities of the surface substances of the specimens cannot influence the reflecting properties of the encapsulated cholesteric liquid crystal.

b) On the surface of all kinds of specimens a 1:4-mixture of cholesteryl 4-carbomethoxyoxybenzoate and cholesteryloleylcarbonate was directly spread and the specimens were placed on the same controlled constant temperature metallic surface as in (a). Pictures were taken at different temperatures, as in (a) (22, 24, 26, 27, 28, 29°C).

In the pictures (Figures 3–9) the cholesteric mixture covering directly the different kinds of specimen surfaces has different colors at the same temperature.

DISCUSSION

From the above mentioned experiments and observations one can conlude that indeed the kind of surfaces used as supports for the mixture of cholesteric liquid crystals and having the same temperature (a) influences the reflected band of visible light from the cholesterics. Precisely:

i) From the series chemically and electrolytically prepared oxides (Figures 3, 4), we see that the reflected band shifts to longer wavelengths for these oxides, as their sorption abilities increase:[24,29]

Sorption ability: Chem. Fe_3O_4 > elect. $Fe_3O_4 \Rightarrow$ refl. wavelength: Chem. Fe_3O_4 > elect. Fe_3O_4 (Figure 3b,v and a,iii).

The same is true for the chem. ZnO and elect. ZnO although they do not have the same color.

Sorption ability: Elect. ZnO > chem. ZnO ⇒ refl. wavelength: Elect. ZnO > chem. ZnO (Figure 4a and b).

ii) In addition to this:

Sorption ability:[12,15,23] γ_2-Al_2O_3 > γ_1-Al_2O_3 > Al ⇒ refl. wavelength γ_2-Al_2O_3 > γ_1-Al_2O_3 > Al (Figure 5c,b and a).

iii) The sensitivity of the method is shown by comparing Figure 6 a,b,c,d, where the reflected band shifts to longer wavelengths ($d \rightarrow a$) from the smaller to the greater thickness following the increase of the sorptive intensity.[12]

iv) According to the slight increase of the sorptive abilities by increasing the preparation current density of γ_1-Al_2O_3,[12] a shift to longer wavelengths ($d \rightarrow a$) is shown in Figure 7a,b,c,d.

v) The greatest sensitivity of this phenomenon is exhibited by the difference between electroplated and mechanically-polished surfaces of the same metal (Figure 8a,b): the reflected band shifts to longer wavelengths ($a \rightarrow b$) on the electroplated metal that has more intense sorption abilities due to numerous and more intense active centers than the mechanically-cleaned metal where the surface geometric active centers were partially eliminated by the treatment:

Sorption ability: Elec. Cu > mec. Cu ⇒ refl. wavelength: Elec. Cu > mec. Cu.

vi) Comparing Figures 9a,b,c,i,ii, 5a,b,c and 9a,b,c,iii it follows that for the same support and liquid crystals mixture the almost general rule that the reflected band shifts to longer wavelengths as the temperature decreases is valid.[1-3]

From these observations it follows that the reflected band by cholesterics shifts to longer wavelengths as their supports are more sorption active.

The quantitative relation between reflected wavelengths by the cholesterics and the sorptive intensity of their supports is the object of a subsequent paper.

On the interpretation of this phenomenon, though much more sensitive, one can temporarily admit the same explanation given for the shifting of the reflected band to longer wavelengths by the cholesterics, increasing the applied pressure,[7] since the sorptive forces are very strong and exceed some hundred bars. The given explanation for the pressure influence[7] is that a shift of the reflected band to longer wavelengths takes place when the conditions lead the system in the neighborhood of a cholesteric to a smectic phase transition. It must be noticed that in the present work the same cholesteric: Cholesteryloleylcarbonate of the same ratio 4:1 as the mixture, in work[7] was used: only the second substance with the smaller percentage is different: cholesteryl 4-carbomethoxyoxybenzoate instead of cholesteryl chloride of the work.[7] But another explanation can also be true based on the quantitative measurements of the reflected band (subsequent paper), taking into account also the electrical forces of the sorptive substances.

The revealed phenomenon itself that: "The supports with their sorption abilities influence the reflected wavelengths by the cholesteric liquid crystals" and the extension of the application for visible reflection of cholesterics, reflecting U.V. light at a certain temperature regions, has a great interest, but there are some other applications that are related to this phenomenon. Precisely the sensibility of the phenomenon permits that the following applications could be developed by measuring the wavelengths of the reflected band:

1) Possibility of collecting data about the structure of the cholesteric mesophase.

2) Finding a method of predicting the sorptive intensity of solids.

3) Predicting the chemical activity of a metal surface and its corrosion tendency, because the reflected wavelength could be a measure of the number and the intensity of the active centers.

4) Predicting the catalytic activity of a solid acting with physical or chemical sorption or by electron exchange.

5) Checking the effectiveness of sand blasting of metal sheets or pipe lines or elements of metallic constructions, since the remaining oxides on their surface regions will give another color to a cholesteric spread on it than on bare surface region.

6) Eventually in other applications too, that we cannot forsee at the present. The experiments for these applications are the subject of subsequent papers.

CONCLUSION

From the above mentioned it follows:

1) Sorptive substances as supports change, at the same temperature, the color of the cholesteric liquid crystals; the reflected light band shifts to longer wavelengths as the sorptive ability of the supports increases.

2) The sensitivity of the method leads to the possibility of identifying the difference of sorptive abilities between the same chemically and electrolytically prepared oxides on metal surfaces. Sharp distinction is also possible between the same electrolytically prepared oxides but with a different secondary structure (γ_1-Al_2O_3, γ_2-Al_2O_3), or thicknesses, or prepared with different current densities. A distinction is also possible between two metal

surfaces, one mechanically cleaned and the other electroplated with the same metal.

3) The rule that the reflected band is usually shifted to longer wavelengths as the temperature decreases is valid for all supports and the cholesteric mixture used.

4) These phenomena result in an extension of the application for visible reflection of cholesterics reflecting U. V. light at a temperature region and to the following possible applications realising quantitative measurements: collecting data on the structure of the cholesterics mesophase, predicting the chemical and catalytical activity of a solid, the corrosion tendency of a metal, checking the effectiveness of sand blasting, etc.

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