Molecular Crystals and Liquid Crystals

Long Term Stability of Cholesteric Liquid Crystal Systems. II

L. C. Scala [a] & G. D. Dixon [a]

[a] Westinghouse Research Laboratories, Pittsburgh, Pa, 15235

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Long Term Stability of Cholesteric Liquid Crystal Systems. II

L. C. SCALA and G. D. DIXON

Westinghouse Research Laboratories
Pittsburgh, Pa. 15235

Abstract—Cholesteric liquid crystal systems exhibiting relatively long useful life in the presence of actinic light were obtained using selected UV absorbers and polymeric protecting media.

1. Introduction

Anisotropic liquid compounds of the cholesteric ester type are used as temperature or electric field sensing devices in industrial and medical applications. However, their use is limited by the fact that, on aging, these sensors lose their characteristic color response, as shown both by loss of intensity and by shifting of their peak reflectance temperature. It has been found[1] that UV radiation and airborne particulate contaminants are in the main responsible for the degradation of the useful properties of sensors made with cholesteric liquid crystals.

This paper extends the investigation on the stability and stabilization of cholesteric liquid crystal systems described previously. It includes the study of additives to eliminate or reduce UV damage and of methods for preparing liquid crystal packages with long useful lives. The effects of bulk aging under different conditions are also reported.

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2. Experimental

The progress of the aging phenomena and of the effects of protectants is generally followed by recording the behavior of the peak

reflectance temperature (obtained using a predetermined optical filter) as a function of time. During this process, the relative color intensity can also be followed semiquantitatively. The apparatus and the test methods used are described in detail in Ref. (1).

Two standard liquid crystal mixtures were used. These were:

(a) oleyl cholesteryl carbonate (OCC) 40: cholesteryl nonanoate (CN) 60,

(b) cholesteryl chloride (CC) 27: OCC 33: CN 40.

The ratios are in parts by weight. Mixture (a) is extremely sensitive to small changes in temperature. Mixture (b) is relatively insensitive to small temperature changes and is used as the sensor in electro-optical devices. All three compounds were obtained from Eastman Chemicals and were carefully purified by successive re-crystallizations until only two peaks were obtained in the DTA.

The samples tested were:

(c) aged films made from (a) and (b) stored in dark,

(d) individual components, after aging, made into films at time of testing,

(e) unaged components made into films at time of testing.†

3. Results

AGING

Aging in Oxygen–Argon Atmosphere

Figure 1 shows the effects of accelerated aging on the OCC-CN mixture in a 45% O_2 in Ar atmosphere under various experimental conditions.

On comparing the behavior of the peak reflectance temperature (5500 Å filter) of the aged samples against that of the refrigerated samples, the deleterious effect of oxygen is readily seen. After 34 weeks of aging, the color response temperatures of all the exposed samples were drastically reduced, while those of the films made from refrigerated ingredients had remained intact.

The same deleterious effect of oxygen is evident in the case of the

† These materials were previously recrystallized and stored in refrigerator.
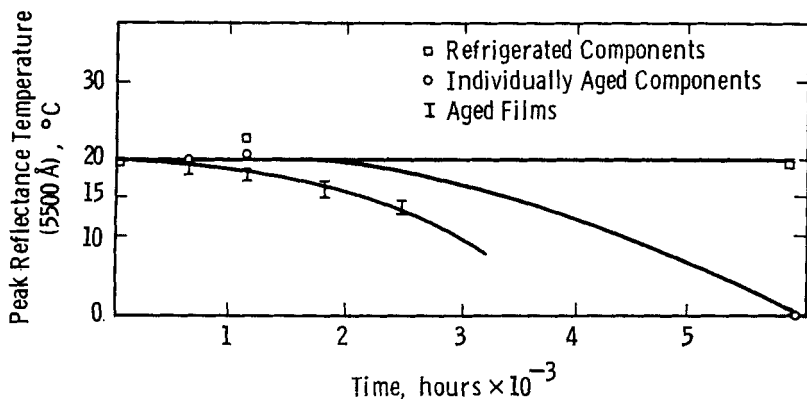
Figure 1. Life of OCC-CN mixture aged in O_2-Ar.

OCC-CC-CN mixture (Fig. 2), although the effect seems less severe in the case of the individually aged components.

Aging in Nitrogen Atmosphere

Films made from mixtures (a) and (b) were aged in 100% N_2 in triplicate. Figure 3 shows that the peak reflectance temperatures of the two mixtures only lose about 2 °C in 40 weeks, indicating that nitrogen gas has no deleterious influence on the color response of the liquid crystals, at the same time reinforcing the conclusion reached above to the effect that oxygen is responsible for the damage shown in Figs. 1 and 2. This result has since been confirmed elsewhere.[2]
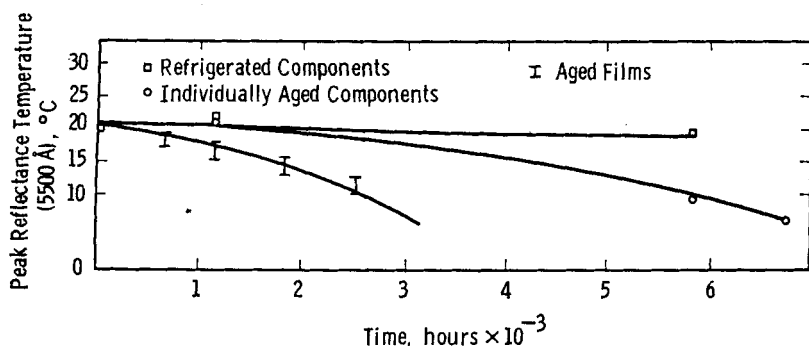
Figure 2. Life of OCC-CN-CC mixture aged in O_2-Ar.

Figure 3. Life of liquid crystal mixtures aged in N_2.

Aging Under Ultraviolet Radiation

Previous work has strongly indicated that damage to the color characteristics of cholesteric liquid crystals exposed to a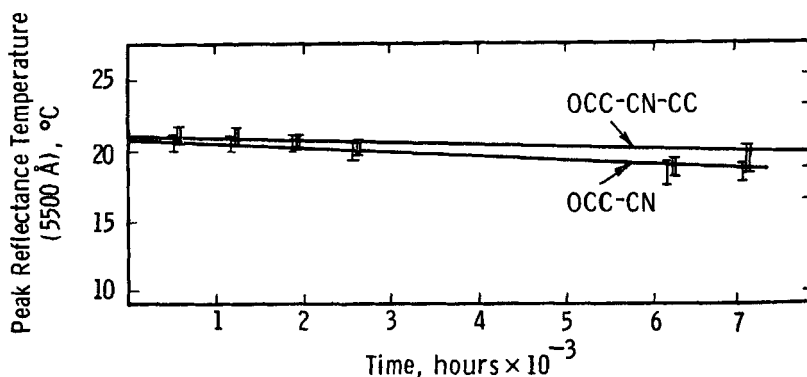rtificial or natural light is in great part due to the effect of ultraviolet irradiation. It was found[1] that exposure to UV light in the presence of air reduced the useful life of liquid crystal films to less than 2 weeks. The same deleterious effect, but to a lesser extent, was observed in irradiated liquid crystal chloroform solutions and, to an even lesser extent, in films made from irradiated ingredients. The very short life of the liquid crystals irradiated in solution was attributed to attack by free radicals formed in the solvent.

Therefore, shielding of cholesteric liquid crystals from UV radiation by the use of UV absorbers was investigated. The test liquid crystal mixture chosen consisted of OCC (33 wt. %), CN (40%), and CC (27%) in a 10% chloroform solution. This system was used because of its possible use as an electro-optical sensor. The UV absorbers listed in Table 1 were added in various percentages to this liquid crystal system and the resulting solutions were cast as thin films (*ca.* 25μ) on a Mylar substrate, placed in a Plexiglas box, and irradiated (Gelman–Camay UV Lamp, Model 51402; 3660 Å; 20 cm distance). The peak reflectance temperatures, using several filters, were measured periodically for each sample and the results for the 5500 Å filter are reported.

Figures 4–7 show the behavior of the peak reflectance temperatures (only 5500 Å shown) as functions of time for the irradiated samples.

TABLE 1   Ultraviolet Absorber Additive Concentrations

Additive		Concentration, wt. %		
A. 4-(Phenyl azo) phenol	1	2	4	5	
B. 4-(4'-Ethoxy phenyl azo) phenyl 10-undecenoate			4	5	6
C. 4-(4'-Ethoxy phenyl azo) phenyl hexanoate			4	5	6
D. Azoxydianisole	1	2	4	5	
E. Cholesteryl 4-(phenyl azo) benzoate			4	5	6
F. Cholesteryl 4-(phenyl azo) phenyl carbonate			4	5	6
G. Benzophenone	1	3	5		

The additives usually altered the initial color response temperatures, B, D, and E raising them and A and G lowering them. Fortuitously, the most effective absorber, C, did not alter the response of the liquid crystal mixture. Table 2 gives the period of time over which the peak reflectance temperatures of the samples changed no more than 2–3 °C or, in other words, a measure of the useful life of the modified samples.

Figure 4 shows clearly the extreme sensitivity of these liquid crystals to UV irradiation; in fact, the useful life of the unprotected system is of the order of 250 hours. Additives A, B, and C (Fig. 5) produce an enormous increase in the useful life of this system under

TABLE 2   Estimated Useful Life of a Cholesteric Liquid
Crystal System Subjected to UV Radiation

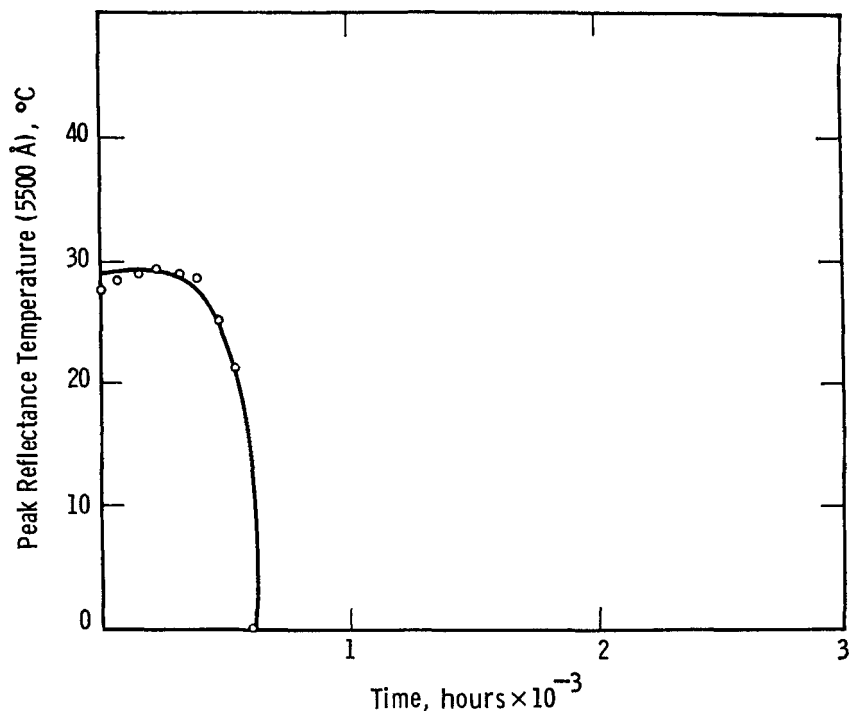| Additive	Time, in hours, before appreciable change in peak reflectance temperature (5500Å) occurs, when exposed to 3660 Å radiation					
	Concentration of additive, wt. %					
	1	2	3	4	5	6
None	250					
A	> 4200	> 4200		> 4200	> 4200	
B				> 4200	> 4200	> 4200
C				> 4200	> 4200	> 4200
D	500	1000		1000	1000	
E				1000	1000	2000
F				50	100	100
G	10		10	10		

Figure 4. Effect of UV irradiation on the response of OCC-CN-CC mixture.

these accelerated aging conditions, being greater than 4200 hours at time of reporting.   Additives D and E (Figs. 6, 7) increase the useful life to about 1000 hours.

The mixture with additive F (Fig. 6), a cholesteryl carbonate ester (cf. cholesteryl oleyl carbonate), has a useful lifetime of the same order as the mixture without a UV absorber.   The cholesteryl carbonate ester molecule is quite unstable, being rapidly oxidized in the presence of O_2.[2]

Benzophenone, additive G, is an active producer of free radicals and causes rapid decomposition of the liquid crystal film (Fig. 7) presumably due to attack on OCC.

Table 3 lists the peak response temperatures (for 5500 Å reflected radiation) of all the combinations investigated, initially, after 1320 hours in a refrigerator, and after exposure to UV radiation for 1224 hours.   This was done to determine any long term effects due to
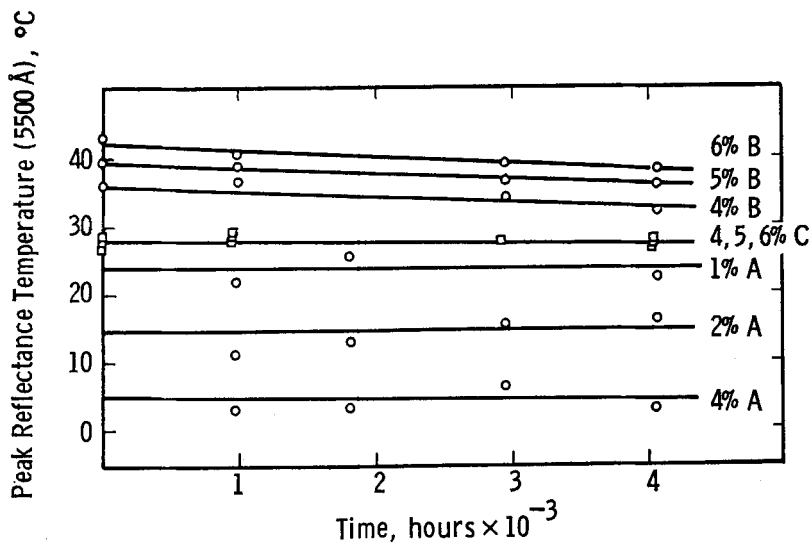
Figure 5. Effect of UV irradiation on life of 3-component LC system with additives A, B and C.
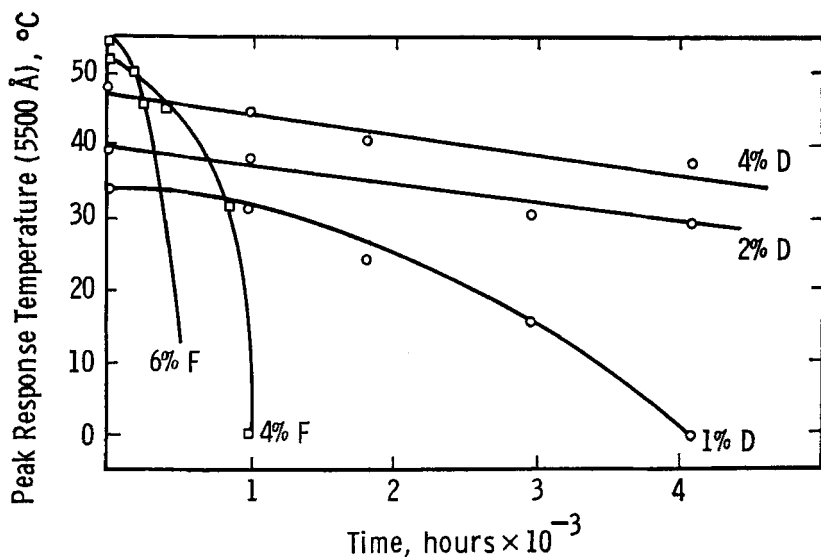

Figure 6. Effect of UV irradiation on life of 3-component LC system with additives D and F.
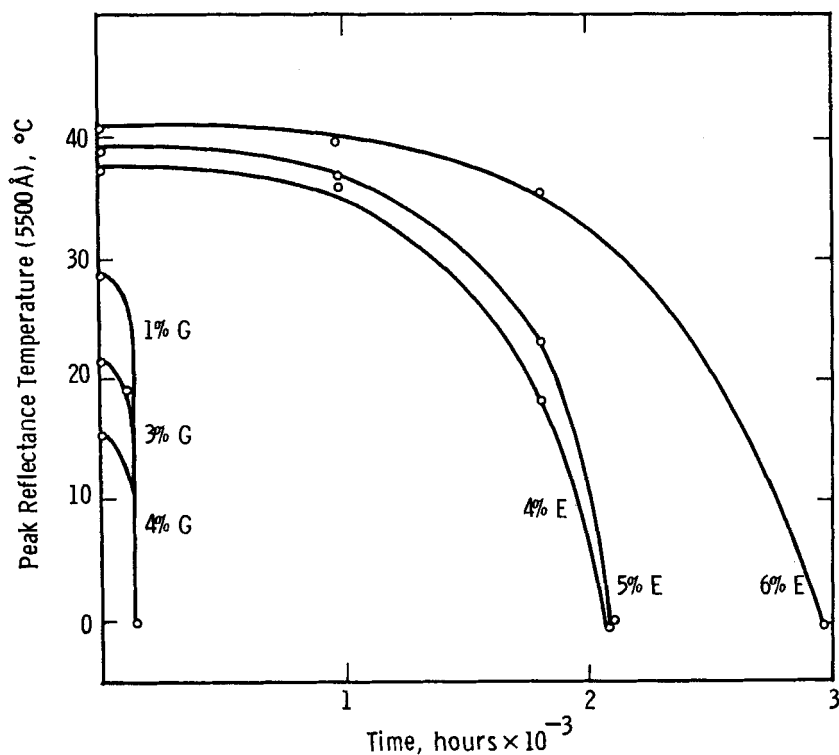
Figure 7. Effect of UV irradiation on life of 3-component LC system with additives E and G.

the additive. In nearly all cases there was no significant difference between the initial response and the response after aging in a refrigerator. [As pointed out elsewhere,[2] the OCC will decompose spontaneously at room temperature, hence the need to refrigerate.]

PROTECTIVE PACKAGING

In the work previously reported,[1] it was shown that the degradation of the useful properties of cholesteric liquid crystals was due not only to the effect of UV irradiation but also to the influence of airborne particulate impurities. It was also found that protecting both sides of a liquid crystal film with Mylar sheets increased the lifetime of the film by preventing textural changes caused by atmospheric contaminants. However, crystalline incongruities in the Mylar

TABLE 3   Responses of an Irradiated Liquid Crystal System
Containing UV Absorbers

Additive	Wt. %	Peak reflectance temperature, °C (5500 Å reflected radiation)		
		Freshly made films	Films aged in refrigerator for 1320 hours	Films irradiated for 1224 hours
None		26.5	27.7	
A	1	15.4	16.1	22.1
	2	8.0	2.0	11.7
	4	−1.5	not measurable†	2.0
	5	−1.5	not measurable†	2.6
B	4	35.8	37.7	36.0
	5	39.5	40.8	39.6
	6	43.0	40.8	39.3
C	4	27.4	28.4	28.0
	5	27.4	28.6	28.0
	6	28.3	27.9	28.9
D	1	33.5	33.1	30.2
	2	39.6	39.9	37.9
	4	48.5	49.2	43.8
	5	52.7	51.6	48.2
E	4	36.9	36.8	31.7
	5	38.9	39.1	34.3
	6	39.8	41.3	38.7
F	4	52.2	51.8	No Response after 1056 hr
	5	53.9	53.4	,, ,, ,, 888 ,,
	6	55.5	56.2	,, ,, ,, 336 ,,
G	1	28.6	25.0	,, ,, ,, 192 ,,
	3	21.5	21.1	,, ,, ,, ,, ,,
	5	15.0	15.0	,, ,, ,, ,, ,,

† There was a great deal of uncertainty concerning temperature responses below 0 °C.

surface may also cause changes in the color response of the liquid crystal film. Therefore, efforts were made to find alternatives to Mylar to circumvent these problems. Table 4 shows the effect on the color response (5000 Å filter) of two OCC-CN mixtures, of approximately the same composition, when packaged with different solid and liquid polymers.

The intensity of the color response in all the cases was not affected by the encapsulants to any appreciable degree.

TABLE 4   Effect of Encapsulants on Color Response of
a Liquid Crystal System

	Film Composition	Peak reflectance temp., °C (5000 Å filter)	Comments
Mixture 1	no additive	36.1	
,, ,,	+ 5% poly γ-benzyl L-glutamate (Pilot Chemicals)	36.5	solid film
,, ,,	+10% poly γ-benzyl L-glutamate	36.9	,, ,,
,, ,,	+5% poly t-butyl isocyanate	35.2	,, ,,
,, ,,	+10% poly t-butyl isocyanate	33.4	,, ,,
Mixture 2	no additive	36.4	
,, ,,	+10% LM Butyl 504 (Enjay Chem. Co.)	36.2	liquid film
,, ,,	+10% R-611 Silicone (70% solids) (Union Carbide)	34.1	,, ,,

Combining the results of the investigations on UV absorbers and
packaging materials should provide a protected liquid crystal sensor
with a greatly increased useful life.   Thus, 4-(4'-ethoxy phenyl azo)
phenyl hexanoate (4.0% by wt. of liquid crystal) was added to a
10% chloroform solution of OCC(40): CN(60).   This mixture is highly
temperature-sensitive and was expected to show changes more
quickly than the mixture containing CC.   Portions of this solution
were mixed with the polymers previously considered then cast into
films.   These films were irradiated (3660 Å, 10 cm distance) and the
changes in color response (for 5500 Å reflected radiation) were
followed.

The test films consisted of:
1. Liquid crystal mixture with UV absorber
    (i) cast from solution onto Mylar films,
    (ii) vacuum sandwiched between Mylar films,
    (iii) cast from a solution containing 7% silicone,
    (iv) cast from a solution containing 10% polybenzyl glutamate.
    (v) cast from a solution containing 5% polybutyl isocyanate.
2. Liquid crystal mixture with no UV absorber and no external
    protection.

All these films were capable of being self supporting except 2.

Figure 8 describes the behavior of the test liquid crystal: UV additive: polymeric mixtures compared with those of a completely untreated mixture and of one that contains only the UV absorber.

The liquid crystal mixture containing no additive lost its color response very rapidly (*ca.* 400 hr), and the liquid crystal mixture with UV absorber but no physical protection (Mylar hoop) also
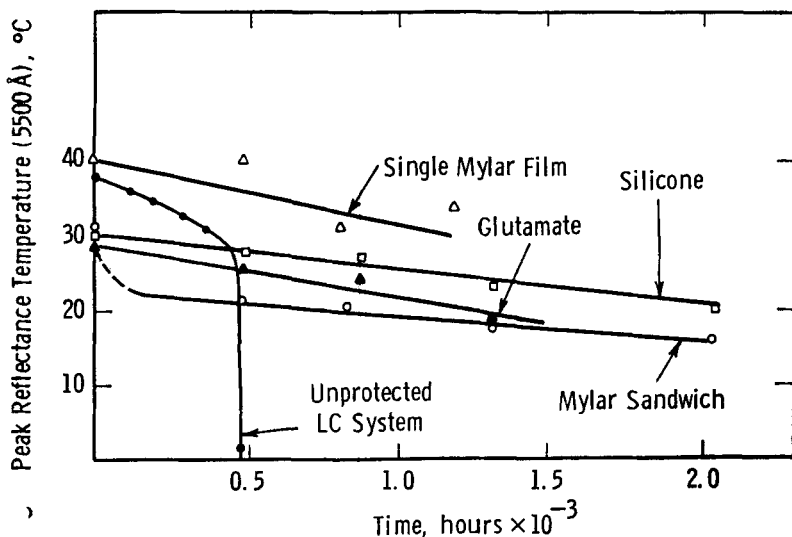

Figure 8. Effect of UV irradiation on the life of a 40:60 OCC:CN mixture containing 4-(4'-ethoxy phenyl azo) phenyl hexanoate in a variety of packaging media.

became inoperative after a relatively short time (*ca.* 700 hr); however, the systems incorporating a fluid silicone, polybenzyl glutamate, or sandwiched between Mylar film exhibited a considerably longer useful life. A system using polybutyl isocyanate as the protecting agent gave poor color response from the beginning and is not shown on the graph.

On the basis of the retention of color intensity and of peak reflectance temperature, the liquid crystal mixture containing the UV additive and protected by the silicone fluid gave the best results.

4. Conclusions

The goal to produce relatively long-lived liquid crystal sensors with useful color responses in both thermal and electrical applications has now been closely approached.   The work reported previously[1] gave substantial indications of the causes for the degradation of the color responses; the present work has attempted to find solutions to such drawbacks by using UV absorbers to eliminate actinic ray damage and by protecting the surface of the liquid crystal systems from the effects of atmospheric contaminants.   This aim was achieved not only with solid or film-like polymers but also with fluid polymers, which probably act as inactive plasticizers and prevent crater formation, the latter reducing the intensity of the color display.

The most effective combination of UV absorber and polymeric protecting media investigated is that involving 4-(4'-ethoxy phenyl azo) phenyl hexanoate and R-611 Silicone (Union Carbide) in the presence of OCC-CN liquid crystal combinations.   This system yields a sensor whose color response temperature changes little (about 4 °C) over about 5 months under conditions of accelerated UV aging. It is known that the basic requirements for a good UV inhibitor are that they must absorb strongly in the 3000–3700 Å range, that they must themselves exhibit long-term stability toward UV light, and that they must dissipate the actinic energy in such a manner as to cause no degradation to the substrate.[3,4,5]   In the systems examined, all the additives absorb 3660 Å radiation to varying degrees.   The more effective absorbers (B and C) absorb most strongly in this region.   The additives containing a carbonate linkage may work the same way as mentioned above but, because of the inherent instability of their carbonate linkage, which slowly breaks down even at R.T. to give off CO_2, exhibit a shorter effective life.   Compounds like benzophenone, well known free radical sources, are unstable under the conditions of our experiments and, in effect, act as accelerators of the breakdown process.

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