

Description

The invention is concerned with cholesteric liquid crystal mixtures consisting of a nematic liquid crystal which is doped with at least two chiral additives.

Cholesteric liquid crystals having a small pitch are used to an increasing extent for various new areas of application, e.g. for polarized light sources [see e.g. Belayev, S.V., et al. In Jpn. J. Appl. Phys. 29, No. 4, (1990), L634] or in order to display temperatures by colour changes of cholesteric layers. It is known that the latter application makes use of the considerable temperature dependence of the helical pitch and hence the selective reflection colour of cholesteric liquid crystals. This enables temperature changes of less than 0.1°C to be displayed by shifting the selective reflective wavelength of a cholesteric layer.

There are applications, however, in which no, or only a slight, temperature dependence of the selective reflection of cholesteric liquid crystals is permissible because a considerable temperature dependence would interfere with or make it impossible to obtain the required effects.

It has already been shown that the temperature dependence of the pitch in the case of chiral nematic mixtures can be reduced by doping them with dextrorotatory and laevorotatory chiral additives [see e.g. Göbl-Wunsch, A. et al. In Zeitschr. Naturforsch. 34a (1979) 594; Gerber, P. Phys. Lett. No. 3 (1980), 285]. These known processes, which result in large-pitch cholesteric liquid crystals, give a compensation of the temperature dependence of the electro-optical properties of nematic field effects.

The use of a similar process to compensate the temperature dependence of the mean value λ_0 of the selective reflection band of cholesteric liquid crystals having a small pitch would be possible only if it were possible to use hitherto unknown dopants and processes for their use.

The object of the invention, therefore, is to indicate liquid crystal mixtures having temperature-compensated selective reflection and a method for producing such a temperature compensation.

This is achieved according to the invention by mixing a nematic liquid crystal material with at least two chiral dopants which satisfy the conditions.

$$(1) \quad a(c_1 B_1 + c_2 B_2) = b(c_1 A_1 + c_2 A_2)$$

and

$$(2) \quad 1/\lambda_o(T) = a(c_1 A_1 + c_2 A_2) + aT(c_1 B_1 + c_2 B_2) + bT(c_1 A_1 + c_2 A_2)$$

where λ_o is the mean value of the wavelength band of the selective reflection $c_1, c_2, \dots$ are the concentrations of the chiral dopants. A_i, B_i are coefficients in the following progression:

$$(3) \quad 1/\lambda_o(T) = \sum_{i=1}^n c_i [A_i + B_i(T-22^\circ\text{C}) + C_i(T-22^\circ\text{C})^2] \cdot [a + b(T-22^\circ\text{C})]$$

The approximation (1) is derived as follows: the temperature dependence of the twisting $1/p$ of a nematic mixture which is doped with a number n of chiral additives of concentrations c_i can be represented as follows:

$$(4) \quad 1/p(T) = \sum_{i=1}^n c_i [A_i + B_i(T-22^\circ\text{C}) + C_i(T-22^\circ\text{C})^2 + \dots]$$

where the coefficients B_i in the linear term essentially indicate the temperature dependence of the twisting. By taking into consideration the temperature dependence of the mean refractive index $\bar{n}(T)$ - which is proportional to the temperature dependence of the nematic degree of order $S(T)$ - in accordance with

$$(5) \quad 1/n(T) = \frac{2n_o(T) + \Delta n(T)}{2} = a + b(T-22^\circ\text{C})$$

where Δn signifies the optical anisotropy and n_o signifies the regular refractive index of the liquid crystal, then for the temperature dependence of the mean wavelength λ_o of planar cholesteric layers consisting of a nematic liquid crystal doped with n chiral additives there is obtained

$$(6) \quad 1/\lambda_o(T) = \sum_{i=1}^n c_i [A_i + B_i(T-22^\circ\text{C}) + C_i(T-22^\circ\text{C})^2] \cdot [a + b(T-22^\circ\text{C})]$$

By disregarding the quadratic and higher powers this equation is reduced for two chiral additives to:

$$(2) \quad 1/\lambda_o(T) = a(c_1A_1 + c_2A_2) + aT(c_1B_1 + c_2B_2) + bT(c_1A_1 + c_2A_2)$$

Since in the present case the pitches of the two chiral additives must have an additive effect to give the small pitch required for the selective reflection in the visible range, the coefficients A_1 and A_2 must have the same sign or must be

$$(7) \quad |c_1A_1 + c_2A_2| \neq 0$$

It thus follows from equation (2) that temperature compensation of λ_o is possible only if two or more chiral additives satisfy the condition

$$(1) \quad a(c_1B_1 + c_2B_2) = b(c_1A_1 + c_2A_2)$$

In the special case in which the temperature dependence of $\bar{n}(T)$ can be disregarded, i.e. at temperatures far below the cholesteric-isotropic phase transition $T \ll T_c$, it follows from equation (1) that the linear temperature coefficients B_i of the two chiral additives have opposite signs and must satisfy the condition $c_1B_1 = c_2B_2$. Alternatively, it is also possible to use chiral additives whose helical pitch temperature dependence is small, or is of a nature such that $\bar{n}(T)$ is just compensated. It is thus also possible to obtain $\lambda_o \neq f(T)$.

Two examples of mixtures which satisfy the above alternatives will be described hereinafter.

Mixture I consists of 76.0 wt.% of a nematic liquid crystal described in detail hereinafter and made up of 26 components and doped with the following dextrorotatory cholesteric additives; in each case the coefficients, A, B and C of formula (3) being given:

5.0 wt.% of diethyl (4S,5S)-2-[trans-4-(p-cyanophenyl) cyclohexyl]-1,3-dioxolane-4,5-dicarboxylate;
 $A = 11.96 \cdot 10^{-2}$, $B = -2.843 \cdot 10^{-4}$, $C = -0.478 \cdot 10^{-6}$

5.1 wt.% of (R)-1-methylheptyl p-[(2S,4R,5S)-5-decyl-4-methyl-m-dioxan-2-yl]benzoate; $A = 14.18 \cdot 10^{-2}$,
 $B = -2.946 \cdot 10^{-4}$, $C = -2.793 \cdot 10^{-6}$

7.5 wt.% of 2,2'-p-phenylenebis[(2S,4R,5S)-4-methyl-5-octyl-m-dioxane]; $A = 13.48 \cdot 10^{-2}$, $B = 0.328 \cdot 10^{-4}$,
 $C = 0.266 \cdot 10^{-6}$

6.4 wt.% of (R)-alpha-methylheptyl 4'-[(2S,4R,5S)-4-methyl-5-octyl-m-dioxan-2-yl]-4-biphenylcarboxylate;
 $A = 14.72 \cdot 10^{-2}$, $B = 1.757 \cdot 10^{-4}$, $C = -1.138 \cdot 10^{-6}$

The nematic liquid crystal is made up as follows:

2.0 wt.% of	4'-ethyl-4-biphenylcarbonitrile
2.0 wt.% of	4'-propyl-4-biphenylcarbonitrile
7.0 wt.% of	4'-pentyl-4-biphenylcarbonitrile
7.0 wt.% of	p-[trans-4-[(E)-1+pentenyl]cyclohexyl]benzonitrile
4.0 wt.% of	p-[trans-[(E)-propenyl]cyclohexyl]benzonitrile
3.0 wt.% of	trans-4-(3-butenyl)-trans-4'-(p-fluorophenyl) [bicyclohexyl]
3.0 wt.% of	trans-4-(p-fluorophenyl)-trans-4'-[(E)-propenyl]- [1,1'-bicyclohexyl]
3.0 wt.% of	4"-pentyl<p-terphenyl>-4-carbonitrile
3.0 wt.% of	4'-[trans-4-(3-butenyl)cyclohexyl]-4-biphenyl- carbonitrile
2.0 wt.% of	4'-[trans-4-[(E)-3-pentenyl]cyclohexyl]-4- biphenylcarbonitrile
2.0 wt.% of	4'-[trans-4-[(E)-propenyl]cyclohexyl]-4-biphenyl- carbonitrile
6.0 wt.% of	1-[2-(trans-4-butylcyclohexyl)ethyl]-4-(trans-4- pentyl cyclohexyl)benzene
4.0 wt.% of	1-[2-(trans-4-butylcyclohexyl)ethyl]-4-[trans-4- (4-pentenyl)cyclohexyl]benzene
3.0 wt.% of	4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4- pentyl-cyclohexyl)-1,1'-ethylenedibenzene
5.0 wt.% of	ethyl p-[2-(trans-4-propylcyclohexyl)ethyl]phenyl ether
6.0 wt.% of	ethyl p-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ether
5.0 wt.% of	4-trans-pentyl-4'-trans-vinyl[1,1'-bicyclohexyl]
6.0 wt.% of	methyl [4'-trans-[(E)-propenyl][1,1'-bicyclohexyl]- 4-trans-yl] methyl ether
4.0 wt.% of	4'-trans-3-butenyl[1,1'-bicyclohexyl]-4-trans-yl ethyl ether
3.0 wt.% of	trans-4-methoxy-trans-4'-[(E)-3-pentenyl]- [bicyclohexyl]
2.0 wt.% of	1-ethoxy-4-[trans-4-[(E)-3-pentenyl]cyclohexyl]- benzene
3.0 wt.% of	(E)-2-butenyl p-(trans-4-propylcyclohexyl)phenyl ether
4.0 wt.% of	(E)-2-butenyl p-(trans-4-pentylcyclohexyl)phenyl ether

3.0 wt.% of	1-ethyl-4'-trans-4-[(E)-3-pentenyl]cyclohexyl]-biphenyl
4.0 wt.% of	1-[trans-4-[(E)-3-pentenyl]cyclohexyl]-4'-propyl-biphenyl
3.0 wt.% of	p-[trans-4-(3-pentenyl)cyclohexyl]phenyl trans-4-propyl-cyclohexanecarboxylate

Mixture II consists of 75.1 wt.% of a nematic liquid crystal described in detail hereinafter and consisting of 24 individual components and doped with the following laevorotatory cholesteric additives; with again for each additive the coefficients A, B and C of formula (3) being given:

3.9 wt.% of	16beta-methyl-17-oxoandrost-5-en-3beta-yl acetate; $A = 12.73 \cdot 10^{-2}$, $B = 4.529 \cdot 10^{-4}$, $C = -0.844 \cdot 10^{-6}$
7.3 wt.% of	bis[(S)-1-methylheptyl] p-terphenyl-4,4"-dicarboxylate; $A = 19.98 \cdot 10^{-2}$, $B = 0.138 \cdot 10^{-4}$, $C = 1.535 \cdot 10^{-6}$
6.9 wt.% of	dibutyl (4R,5R)-2-[trans-4-(p-cyanophenyl)cyclohexyl]-1,3-dioxolane-4,5-dicarboxylate; $A = 8.912 \cdot 10^{-2}$, $B = 0.342 \cdot 10^{-4}$, $C = 1.038 \cdot 10^{-6}$
6.8 wt.% of	diethyl (4R, 5R)-2-[trans-4-(p-cyanophenyl)cyclohexyl]-1,3-dioxolane-4,5-dicarboxylate; $A = 11.66 \cdot 10^{-2}$, $B = 2.862 \cdot 10^{-4}$, $C = -0.562 \cdot 10^{-6}$

The nematic liquid crystal is made up as follows:

3.0 wt.% of	4'-ethyl-4-biphenylcarbonitrile
3.0 wt.% of	4'-propyl-4-biphenylcarbonitrile
5.0 wt.% of	4'-pentyl-4-biphenylcarbonitrile
4.0 wt.% of	p-[trans-4-(3-butenyl)cyclohexyl]benzonitrile
8.0 wt.% of	p-[trans-4-[(E)-1+pentenyl]cyclohexyl]benzonitrile
3.0 wt.% of	4"-pentyl<p-terphenyl>-4-carbonitrile
3.0 wt.% of	4'-[trans-4-(3-butenyl)cyclohexyl]-4-biphenylcarbonitrile
2.0 wt.% of	4'-[trans-4-[(E)-3-pentenyl]cyclohexyl]-4-biphenylcarbonitrile
8.0 wt.% of	1-[2-(trans-4-butylcyclohexyl)ethyl]-4-(trans-4-pentylcyclohexyl)benzene
2.0 wt.% of	5-(trans-4-pentylcyclohexyl)-2-[p-(trans-4-propylcyclohexyl)phenyl]pyrimidine

3.0 wt.% of	4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4-pentyl-cyclohexyl)-1,1'-ethylenedibenzene
3.0 wt.% of	p-cyanophenyl trans-4-[2-(trans-4-propylcyclohexyl)ethyl]cyclohexanecarboxylate
7.0 wt.% of	ethyl p-[2-(trans-4-propylcyclohexyl)ethyl]phenyl ether
10.0 wt.% of	ethyl p-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ether
6.0 wt.% of	4-trans-pentyl-4'-trans-vinyl[1,1'-bicyclohexyl]
5.0 wt.% of	4'-trans-(3-butenyl)[1,1'-bicyclohexyl]-4-trans-yl ethyl ether
3.0 wt.% of	4'-trans-(4-pentenyl)[1,1'-bicyclohexyl]-4-trans-yl ethyl ether
3.0 wt.% of	trans-4-methoxy-trans-4'-[(E)-3-pentenyl]-[bicyclohexyl]
2.0 wt.% of	1-ethoxy-4-[trans-4-[(E)-3-pentenyl]cyclohexyl]-benzene
3.0 wt.% of	(E)-2-butenyl p-(trans-4-propylcyclohexyl)phenyl ether
4.0 wt.% of	(E)-2-butenyl p-(trans-4-pentylcyclohexyl)phenyl ether
3.0 wt.% of	1-ethyl-4'-[trans-4-[(E)-3-pentenyl]cyclohexyl]-biphenyl
4.0 wt.% of	1-[trans-4-[(E)-3-pentenyl]cyclohexyl]-4'-propyl-biphenyl
3.0 wt.% of	p-[trans-4-(3-pentenyl)cyclohexyl]phenyl trans-4-propyl-cyclohexanecarboxylate

The measured properties of the two mixtures I and II are compiled in the following Table:

Parameter	Mixture I	Mixture II
λ_o [nm]	470	470
$\Delta\lambda_{FWHM}$ [nm]	35	35
$d\lambda_o/dT$ [nm/°C]	0.10	-0.10
A [nm/wt.%]	6.02	6.02
n_o	1.498	1.496
Δn	0.120	0.110
Temperature range [°C]	0 - 50	0 - 50
T_o [°C]	57	63
Direction of helical rotation	L	R

In this Table λ_o signifies the mean wavelength of the selective reflection; $\Delta\lambda_{FWHM}$ signifies the bandwidth of the selective reflection (FWHM = full width at half maximum); $d\lambda_o/dT$ signifies the temperature dependence of λ_o in the operating temperature range; A indicates a coefficient which indicates the increase of $\lambda_o(c)$ due to the doping of the cholesteric mixture with its nematic "host" substance in accordance with the following formula: $\lambda_o(c) = \lambda_o + Ac$; T_o signifies the cholesteric-isotropic transition temperature.

Claims

1. A cholesteric liquid crystal mixture consisting of a nematic liquid crystal which is doped with at least two chiral additives and is characterized in that the chiral additives satisfy the conditions

$$(1) \quad a(c_1B_1 + c_2B_2) = b(c_1A_1 + c_2A_2)$$

and



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Claims

1. A cholesteric liquid crystal mixture consisting of a nematic liquid crystal which is doped with at least two chiral additives and is characterized in that the chiral additives satisfy the conditions

$$(1) \quad a(c_1B_1 + c_2B_2) = b(c_1A_1 + c_2A_2)$$

and



$$(2) \quad 1/\lambda_o(T) = a(c_1A_1 + c_2A_2) + aT(c_1B_1 + c_2B_2) + bT(c_1A_1 + c_2A_2)$$

and therewith the selective reflection of the entire mixture is temperature compensated and $d\lambda_o/dT < 0.5 \text{ nm}/^\circ\text{C}$ applies over the operating temperature range of the mixture, where λ_o is the mean value of the wavelength band of the selective reflection, $c_1, c_2, \dots$ are the concentrations of the chiral dopants and A_i, B_i are coefficients in the following progression

$$(3) \quad 1/\lambda_o(T) = \sum_{i=1}^n c_i [A_i + B_i(T - 22^\circ\text{C}) + C_i(T - 22^\circ\text{C})^2] \cdot [a + b(T - 22^\circ\text{C})]$$

2. A method for the temperature compensation of the wavelength-selective reflection of a cholesteric liquid crystal using at least two chiral dopants, characterized in that the dopants satisfy the conditions

$$(1) \quad a(c_1B_1 + c_2B_2) = b(c_1A_1 + c_2A_2)$$

and

$$(2) \quad 1/\lambda_o(T) = a(c_1A_1 + c_2A_2) + aT(c_1B_1 + c_2B_2) + bT(c_1A_1 + c_2A_2)$$

where λ_o is the mean value of the wavelength band of the selective reflection, $c_1, c_2, \dots$ are the concentrations of the chiral dopants and A_i, B_i are coefficients in the following progression

$$(3) \quad 1/\lambda_o(T) = \sum_{i=1}^n c_i [A_i + B_i(T - 22^\circ\text{C}) + C_i(T - 22^\circ\text{C})^2] \cdot [a + b(T - 22^\circ\text{C})]$$

and $d\lambda_o/dT < 0.5 \text{ nm}/^\circ\text{C}$ applies over the operating temperature range of the mixture.