

Similar inspection of electronic components can be conducted to detect flaws and failures in fabrication. Further, the attractive color patterns of very precise delineation prove useful in several areas for their decorative, intrigue and colorfulness. Such areas include decorative panels for offices and aircraft interiors and toys which have psychological attractiveness to children because of their variety of color display when touched by a human hand.

To fabricate a toy or a decorative color panel, ^{They} ~~we~~ have applied approximately 0.5 gram of any of the above compositions, with filler additions, to a sheet of clear acetate, Mylar or Plexiglass typically by spreading the cholesteryl medium by manual means. A second sheet of clear film material is placed over the clear sheet coated with the mixture. The sandwich is then placed between two metal blocks of approximately the same area as the sandwich. These blocks are heated to approximately 40-60°C. and exert a force of an order of 5 lbs. on the sandwich. The metal blocks on the sandwich are then placed in a vacuum of about 10 mm. Hg. After about one minute at this pressure, air is admitted to the chamber rapidly. The above procedure has been successful in producing a thin, uniform film of liquid crystals sandwiched between the protective layers mentioned above. To prevent slippage of the protective layers, we have investigated the following methods of sealing, any of which would be feasible with

the above-mentioned materials : (a) tape, (b) adhesive, (c) ultrasonic sealing and (d) thermal sealing. Another method of sealing the toy makes use of a sandwich of vinyl materials sealed on three edges. An excess of liquid crvatnl material is injected into the envelope at the narrow end which remains open. The sandwich is then passed between variable pressure rolls heated to 40-50°C. This forces the air out of the envelope and spreads the liquid crvstals uniformly. The open end of the envelope is then sealed thermally to close the container. This has worked quite well with small test samples and can be readily adapted to large scale productions.

Large sandwiches of compositions of the liquid crystals set forth above can be made using vsrly thin (0.001 inch) film to permit inspection of surfaces without necessity of painting the surfaces with liquid crystal compositions. To produce these thin films, ^{They} I used a vacuum frame to draw Saran wrap or Teflon film very tight and then paint the composition of liquid crystal upon the Saran wrap or Teflon film. The first Saran wrap or Teflon film is then cut to the inner dimensions of the vacuum frame and a second film is placed on the frame. When the frame is re-evacuated, the second film is pressed against the liquid crystalline composition and forms an air-free sandwich. The sandwich can then be placed on a surface to reinspect it and reuse repeatedly.

Essentially the same process has been used in preparing larger panels of Plexiglas with the above compositions of liquid crystals deposited between the cover sheets thereof. By selectively or randomly heating portions of the panels, some very artistic effects can be gained from the color patterns exhibited by the panels.

Application 13

HYSTERETIC CHOLESTERIC LIQUID CRYSTALLINE COMPOSITIONS
AND RECORDING DEVICES UTILIZING SUCH COMPOSITIONS

It has been discovered, and the present invention is in large part based on this discovery, that certain liquid crystal cholesteric compositions may be formulated to provide a significant color change time lag after the change from the liquid phase to the cholesteric phase. Such hysteretic compositions may be employed, for example, to determine not only whether a given temperature has been exceeded but also to provide a record, for a significant time period, of whether the temperature has been exceeded. The lag in color change will also occur if the compositions have been exposed to high intensity electric fields in the order of 20 volts per micron or to gas vapors, such as vapors of chloroform in concentrations in the order of 100 p.p.m. in air.

It is apparent, of course, that not all cholesterogenic materials are hysteretic in their color transformations. Indeed, most of the heretofore known materials rapidly change color in response to environmental changes. The mixtures or combination of compounds of this invention return to their colored state, from a colorless liquid phase, only after a time delay in the order of 3 to 30 minutes. Moreover the mixtures will have bright visible colors in the aligned cholesteric phase and will not crystallize in the range of

normal temperatures, i.e. 0°F . So 300°F . The particular substrate employed, whether glass, polyester or some other clear plastics film, will have some effect ON the actual color change delay time for a particular composition but the time delay phenomenon will be observed on all substrates.

The hysteretic liquid crystalline cholesteric mixtures of this invention contain (A) from 15 to 40 percent, by weight, of at least one halide selected from the group consisting of cholesteryl chloride, cholesteryl bromide, cholesteryl iodide, cholestanyl chloride, cholestanyl bromide and cholestanyl iodide and (B) at least 30 percent by weight, of at least one compound selected from the group consisting of cholesteryl erucyl carbonate, cholestanyl erucyl carbonate, cholesteryl oleyl carbonate, cholestanyl olcyl carbonate, cholesteryl erucate, cholestanyl erucate, cholesteryl oleate and cholestanyl oleate.

Referring now to Fig.1, there is illustrated as one example of the invention a simplified temperature recording or information storing device 10 that includes a clear sheet of polyethylene terephthalate 11 having a thickness of approximately 6 microns. A pigmented film 12 containing carbon black dispersed in a layer of polyvinyl alcohol and having a thickness of approximately 12 microns is deposited on one side of the terephthalate film 11. The film 12 is applied as an aqueous solution or suspension

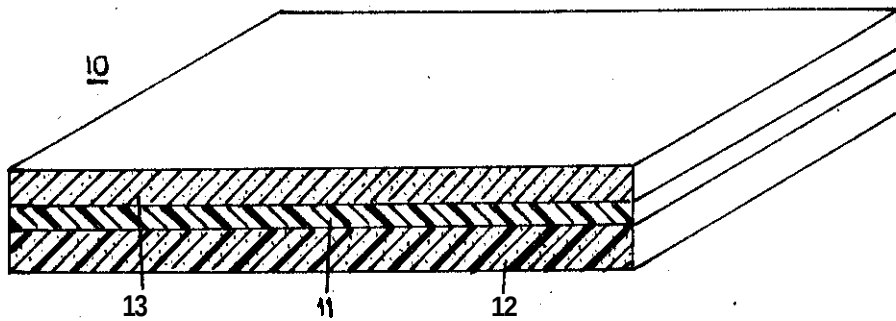


FIG 1

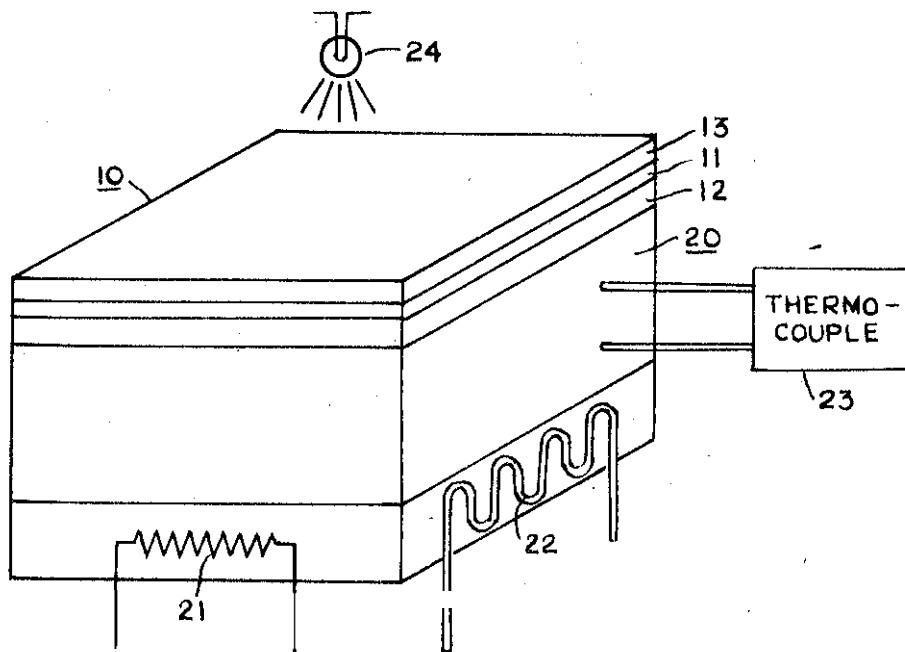


FIG. 2

and dried on the film 11. A film of the hysteretic liquid crystalline cholesteric mixture 13 having a thickness of approximately 10 microns is deposited on the other side of the terephthalate base 11. The film 13 is deposited by applying a 10 percent solution of the hysteretic mixture in petroleum ether onto the film 11 and evaporating the solvent.

As an illustration of the practice of the invention, there is shown in Fig. 2, the recording device 10 placed so that film 12 is in intimate contact with an aluminum plate or block 20. The block 20 is adapted to be heated, as for example, by a resistance heater 21, and is adapted to be cooled either by lower ambient temperatures after the heating has ceased or by cooling means such as the coil 22 containing circulating cold water. A thermocouple P3 is embedded in the plate 20 so that an accurate measurement of the temperatures of the block can be made. A source of white light 24 is provided so that the color of the layer of hysteretic film in the device will be visible to the naked eye. The visible color is, of course, a known phenomenon associated with the light scattering properties of the cholesteric phase.

EXAMPLE I

A series of simple recording devices were prepared, in the manner described hereinabove in conjunction with Fig. 1,

using for film 13 a variety of simple admixtures of combinations of compounds in accordance with the constituent mixtures and composition ranges set forth above for the preparation of suitable hysteretic compositions. These simple devices were then placed in contact with the aluminum plate 20 of Fig.2 and heated until there was a transformation from the cholesteric phase to the liquid phase. The phase transformation was apparent as the layer was observed to change from a vivid color to a colorless layer.

When the layer was cooled, it reverted to the cholesteric phase but the color returned only after a significant delay in time. The compositions presented in Table I hereinbelow were found to be hysteretic and there, their room temperatures colors, i.e. the color of the cholesteric phase, and their clearing points, i.e. the melt point or liquid transition point, were as indicated. In each case, at least a three minute time lag was observed in the color change, after the layer had been cooled to a temperature where the material was in the cholesteric phase. All of the percentages in the table below and those that appear thereafter are weight percentages unless otherwise specified.

TABLE 1. PROPERTIES OF HYSTERETIC MIXTURES

Example Number	Composition	Color of Cholesteric phase	Clearing point, °C
1	30 percent cholesteryl Chloride 70 percent Cholesteryl Erucate	Red	37.5
2	20 percent Cholesteryl Chloride 80 percent Cholesteryl Erucate	Green	38.2
3	15 percent Cholesteryl Chloride 85 percent Cholesteryl Erucate	Blue	40
4	24 percent Cholesteryl Chloride 76 percent Cholesteryl Oleyl Carbonate	Green	45
5	20 percent Cholesteryl Chloride 80 percent Cholesteryl Oleyl Carbonate	Blue	45.4
6	30 percent Cholesteryl Chloride 70 percent Cholesteryl Oleyl Carbonate	Red	46
	26 percent Cholesteryl Bromide 74 percent Cholesteryl Oleyl Carbonate	Green	43.8
8	26 percent Cholesteryl Bromide 74 percent Cholesteryl Oleate	Green	41.1
9	26 percent Cholesteryl Chloride 74 percent Cholesteryl Erucyl Carbonate	Green	38.6

It should be understood that the foregoing are examples and that other film thickness and mixtures may be employed. Glass or other clear plastic films may be employed in place of the polyethylene terephthalate film. Other pigments e.g. gold black, may be substituted for the carbon black. The pigment may be dispersed in methyl cellulose, polyvinyl pyrrolidone or other plastic materials in place of the polyvinyl alcohol. The color of the pigment should be complementary to the color of the light beam directed onto the hysteretic cholesteric layer. When the incident light is white, the pigment should be black, and when the light is red, the pigment should be green. The cholesteric layer may be deposited from other volatile organic solvent such as chloroform, halogenated hydrocarbons and volatile hydrocarbon solvents. The cholesteric layer need only be a few microns in thickness but may be in the order of 50 microns and more. It should also be understood that cholesteryl compounds may be substituted for the foregoing cholesteryl compounds to provide similar results.

As is apparent from the data in Table I, only a small variation in the clearing point occurs with varying amounts of compounds in a given combination of compounds. It has also been discovered however, that significant changes in clearing points may be made by the addition of certain clearing point modulating agents. Up to 35 percent, by weight, of (C) a clearing point elevating agent selected from the group of esters consisting of cholesteryl nonanoate, cholesteryl nonanoate, cholesteryl decanoate and

cholestanyl decanoate may be included in the admixtures of compounds (A) and (B) to raise the clearing point temperature of the deposited cholesteric layer. The hysteretic effect is present in the layer even though the ester has been added to raise the clearing point. However, the total amount of materials or compounds selected from (A) and (C) should not exceed 60 percent of the weight of the total mixture.

As little as 1.0 percent of the esters in the group (C) will have a noticeable and useful effect in elevating the clearing point temperature of a basic mixture (A) and (B). In general, the addition of about 5 percent of any of the esters (C) will raise the clearing point about one degree centigrade.

EXAMPLE II

Referring again to the device 8 shown in Fig. 1, admixtures containing the compounds (A), (B) and the described esters (C) were employed to form the recording device 10 by depositing the admixture as a 10 micron thick layer 13 from a ten percent solution in petroleum ether onto one side of a 6 micron Chfak polyethylene terephthalate film 11. The other side of the film 11 had the pigmented layer 17 described hereinbefore. Recording devices, with the compositions described in Table II providing the hysteretic liquid crystalline cholesteric layers, were tested in the apparatus of Fig. 2 in the manner heretofore described in conjunction with the example of Table I. Again, at least a three minute time lag was observed in the color change

after the layer was cooled below its clearing point. That the esters (C) have a pronounced and predictable effect in elevating the clearing point of a basic mixture of a hysteretic cholesteric composition of (A) and (9) is apparent from the data of Table II.

It should be understood that cholesteryl nonanoate and decanoate may be substituted for the cholesteryl nonanoate and decanoate in the examples shown in Table II with similar results. Some variation in the actual clearing point may occur for identical amounts of ester (C) in any hysteretic composition and the clearing points may be readily calibrated for the particular ester being employed. It should also be understood that both the cholesteryl and cholestanyl esters of the group (C) may be employed with either the cholestanyl and /or cholesteryl compounds of the groups (A) and (B).

TABLE II ELEVATION OF CLEARING POINT

Example Number	Composition	Color of Cholesteric phase	Clearing Point ^o
10	28 percent Cholesteryl Chloride	Red	51
	26 percent Cholesteryl Nonanoate		
	46 percent Cholesteryl Oleyl Carbonate		
11	28 percent Cholesteryl Chloride	Red	44
	10 percent Cholesteryl Nonanoate		
	62 percent Cholesteryl Oleyl Carbonate		
12	28 percent Cholesteryl Chloride	Red	51
	26 percent Cholesteryl Decanoate		
	46 percent Cholesteryl Oleyl Carbonate		
13.	28 percent Cholesteryl Chloride	Red	44
	10 percent Cholesteryl Decanoate		
	62 percent Cholesteryl Oleyl Carbonate		

In order to depress the clearing point of a given mixture of (A) and (B), up to about 10 percent of another class of modulating agents (D), in this instance known as depressing agents, may be included in the mixture. Fatty compounds which dissolve the admixture (A) and (B) without crystallizing will function as clearing point depressing agents. Suitable fatty compounds for this purpose include the fatty acids, fatty esters and fatty alcohols, both saturated and unsaturated hydrocarbon acids with preferably over 8 carbon atoms, for example, oleic, stearic, palmitic, lauric, erucic, myristic and behenic acids. Suitable fatty esters are derived by reacting monohydric and polyhydric hydrocarbon alcohols, with the fatty acids, for example, methyl oleate, ethyl oleate, cetyl oleate, diolein, triolein, tributrin, tripalmitin, tristearin and mixtures thereof, particularly mixtures of triglyceryl esters of fatty acids such as the naturally occurring olive, sperm, soybean, corn and tall oils. Suitable fatty alcohols are, for example, oleyl, stearyl, cetyl and lauryl alcohols. The liquid fatty compounds are preferred but the solid compounds may be employed, if the ultimate admixture with the combination of (A) and (B) does not crystallize. Crystallization will, of course, destroy the liquid crystal cholesteric phase.

EXAMPLE III

Again referring to Fig.1, admixtures containing the compounds (A), (B) and the fatty compounds (D) were employed to form the simple recording device 20 by depositing various admixtures as a 10 micron thick layer 13 from a ten percent solution in petroleum ether onto one side of a 6 micron thick polyethylene terephthalate film 11. The other side of the film 11 had the pigmented layer 12 described hereinabove. Recording devices, with the compositions described in Table III hereinbelow being deposited as the hysteretic liquid crystalline cholesteric layers, were tested in the apparatus of Fig.2 in the manner heretofore described. Again, at least a three minute time lag was observed in the color change after the various layers were cooled to temperatures below their clearing points. That the fatty compounds (D) have a predictable effect in depressing the clearing point of a basic mixture of a hysteretic composition of (A) and (B) is apparent from Table IT?

TABLE III DEPRESSION OF CLEARING POINT

Example Number	Composition	Color of Cholesteric Phase	Clearing Point °C.
14	26 percent Cholesteryl Chloride 73 percent Cholesteryl Oleyl Carbonate 1 percent Oleic Acid	Green	36.4
15	26 percent Cholesteryl Chloride 72 percent Cholesteryl Oleyl Carbonate 2 percent Oleic Acid	Green	35.3

Example Number	Composition	Color of Cholesteric Phase	Clearing Point °C
16	26 percent Cholesteryl Chloride 71 percent Cholesteryl Oleyl Carbonate 3 percent Oleic Acid	Green	36.4
17	26 percent Cholesteryl Chloride 73 percent Cholesteryl Oleyl Carbonate 1 percent Methyl Oleate	Green	33.4
18	26 percent Cholesteryl Chloride 71 percent Cholesteryl Oleyl Carbonate 2 percent Methyl Oleate	Green	38
19	26 percent Cholesteryl Chloride 71 percent Cholesteryl Oleyl Carbonate 3 percent Methyl Oleate	Green	33
20	26 percent Cholesteryl Chloride 73 percent Cholesteryl Oleyl Carbonate 1 percent Triolein	Green	36.5
21	26 percent Cholesteryl Chloride 72 percent Cholesteryl Oleyl Carbonate 2 percent Triolein	Green	35.8
22	26 percent Cholesteryl Chloride 71 percent Cholesteryl Oleyl Carbonate 3 percent Triolein	Green	33.5
23	26 percent Cholesteryl Chloride 73 percent Cholesteryl Oleyl Carbonate 1 percent Oleyl Alcohol	Green	36
24	26 percent Cholesteryl Chloride 72 percent Cholesteryl Oleyl Carbonate 2 percent Oleyl Alcohol	Green	35
25	26 percent Cholesteryl Chloride 71 percent Cholesteryl Oleyl Carbonate 3 percent Oleyl Alcohol	Green	33
26	26 percent Chloride 73 percent Cholesteryl Oleyl Carbonate 1 percent Olive Oil	Green	36.5
27	26 percent Cholesteryl Chloride 72 percent Cholesteryl Oleyl Carbonate 2 percent Olive Oil	Green	35.5
28	26 percent Cholesteryl Chloride 71 percent Cholesteryl Oleyl Carbonate 3 percent Olive Oil	Green	33.5

Example Number	Composition	Color of Cholesteric Phase	Clearing Point °C
29	26 percent Cholesteryl Chloride 72 percent Cholesteryl Oleyl Carbonate 1 percent Sperm Oil	Green	36
30	26 percent Cholesteryl Chloride 72 percent Cholesteryl Oleyl Carbonate 2 Sperm Oil	Green	38
31	26 percent Cholesteryl Chloride 71 percent Cholesteryl Oleyl Carbonate 3 percent Sperm Oil	Green	33
32	26 percent Cholesteryl chlorine 73 percent Cholesteryl Oleyl Carbonate 1 percent Tributrin	Green.	35.5
33	26 percent Cholesteryl Chloride 72 percent Cholesteryl Oleyl Carbonate 2 percent Tributrin	Green	34.5
34	26 percent Cholesteryl Chloride 71 percent Cholesteryl Oleyl Carbonate 3 percent Tributrin	Green	32.5

It should be understood that the depressing agents may be employed with the cholestanyl compounds as well as the cholesteryl compounds. Other fatty compounds may be substituted for those employed in the examples of Table XIX with equivalent results although some variations in the actual clearing point may occur. Again, calibration for the particular modulating agent being employed is recommended. The clearing point, in general, will be depressed from about 1 to 2 degrees centigrade for each weight percent of fatty compound in the admixture. As little as 0.1 percent of the fatty compound will provide a perceptible change in the clearing point of a particular admixture.

As noted heretofore, the device of Fig.1 so long as it has a layer of hysteretic cholesteric liquid crystalline material, will function as a temperature recording device for the environment contacting the device. The device may be calibrated by the selection of a proper hysteretic film composition, to determine and record whether a particular temperature has been exceeded.

All of the heretofore described hysteretic compositions may be employed as thin films in devices which will record or store information on environmental conditions other than temperature. Again referring to Fig.1., a 10 micron layer of a composition containing 28 percent cholesteryl chloride and 72 percent cholesteryl oleyl carbonate is deposited as the layer or film 13, the substrate sheet 11 and the pigmented film or layer 12 being as heretofore described in Example I. Such a device 10 will have an easily visible pronounced color at room temperature when exposed to white light. If a 200 volt per cm. field is applied across the 10 microns hysteretic cholesteric layer 13, the color will disappear and the layer will become colorless. The layer 13 will remain clear for about 3 weeks if it is not heated through its clearing point.

The same device may, instead, be employed to record the presence of contaminating vapors, for example. When exposed to air containing from 70 to 100 ppm. of either chloroform or trichloroethylene, the color will disappear. The hysteretic layer will remain colorless for about 10 minutes after it is removed from the contaminating atmosphere

Application 14

A VISUAL DISPLAY DEVICE

This invention relates to temperature-sensitive visual display devices and, more specifically, relates to such devices in the form of a dried emulsion coating having incorporated droplets of cholesteric mesomorphic (liquid crystal) material, which material changes in iridescent characteristics where and when temperature changes occur on the coating.

In the specification of United Kingdom Patent No. 1,138,590 a display device is disclosed and claimed which includes an array of minute polymeric capsules containing cholesteric mesomorphic material and adhered to a substrate whose temperature pattern is to be displayed.

While somewhat related to the use of the above-mentioned capsule arrays, an emulsion of unencapsulated cholesteric mesomorphic material, which is part of the subject matter of this invention, is vastly different from those other disclosures in several important respects. The droplets of the material of this invention are not encapsulated but are inclusions in the continuous phase of the emulsion. The emulsion, or coating liquid, of this invention can be prepared by a simple and inexpensive, one-step process, thereby obviating the necessity for complex capsule-manufacturing equipment and techniques with attendant high manufacturing costs. The emulsion of this invention,

when dried nt a coating *On* a body whose temperature pattern is to be displayed, provides thrt incident light be transmitted through only a single kind of material in order to be reflected iridescently from the unencapsulated droplets of cholesteric mesomorphic material. Due to the extremely small droplet size which can be maintained in an emulsion of unencapsulated droplets of the cholesteric mesomorphic materials, coatings prepared from an emulsion permit of a high degree of optical resolution and also have a very smooth surface.

Figure 1a is a diagrammatic edge view of a substrate sheet 10 having, on one surface, a coating of minute droplets 11 of liquid crystalline material dispersed in a matrix-like polymeric binder material 12, the liquid crystal material being shown in either the isotropic liquid state or the crystalline solid state; that is, not in the mesomorphic state. 45 percent by weight, cholesteryl nonanoate and had a color producing temperature, in the upward excursion, of about 33 degree Centigrade. The temperature range of color response for this mixture was from about 33 degrees Centigrade to about 35.5 degrees Centigrade. Three parts, by weight, of the above mixture of liquid crystal material were emulsified in a Waring Blender with five parts, by weight, of a 10 percent by weight, aqueous solution of poly (vinyl alcohol) described below, until a liquid crystal droplet size-range of from about five

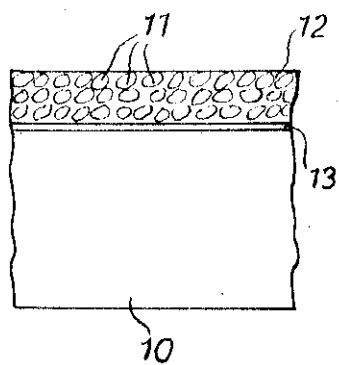


FIG 1a

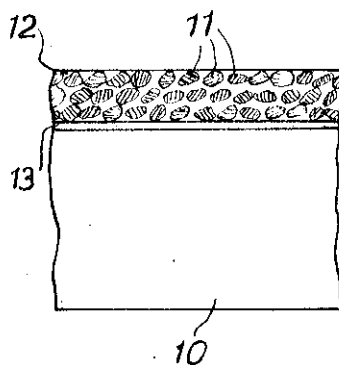


FIG 1b

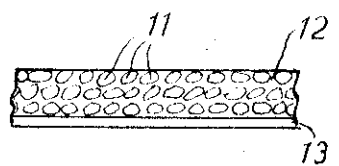


FIG. 2

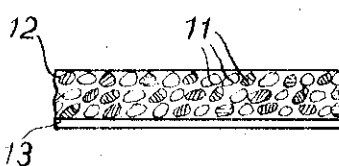


FIG. 3

microns to about twenty microns was obtained. The poly (vinyl alcohol) used in this example has an average molecular weight of 88,000 and was characterized by the facts that (a) a 4 percent, by weight, aqueous solution of the material exhibited a viscosity of 2.3 to 2.8 centipoises at 25 degrees Centigrade, and (b) the material was 97.7 percent to 98.4 percent hydrolyzed; that is, that specified percentage of acetate chemical groups originally present in molecules of the subject material had been converted to hydroxyl groups.

The emulsion, once prepared, was coated by means of a draw-down applicator to a wet-film thickness of about ten mils onto a blackened substrate sheet of polyethylene terephthalate. The film was allowed to dry in air at about 25 degrees Centigrade. If the temperature of the coating was raised at a point, concentric rings representing a temperature gradient in the range of from 33 degrees Centigrade to 35.5 Degrees Centigrade appeared outwardly from a central ring of blue, thence spectrally in order through red, as the temperature gradient decreased. As the temperature of the point was increased or decreased, the effect was evidenced by expansion or contraction of the rings. Systems of adjacent expanding and contracting rings from two or more points intersected, and the resultant colors of an area was a function of the temperature of that area. The dried emulsion film of this example

can be stripped from its polyethylene terephthalate substrate and utilized as an unbacked film. It is displaying temperature gradient patterns. The striped film can be blackened or opacified on one surface, or it can be used without such blackener or opacifier, as desired.

EXAMPLE II

In this example, a mixture of liquid crystal material was used which consisted of 80 percent, by weight, oleyl cholesteryl carbonate and 20 percent by weight, cholesteryl nonanoate. Three parts of the liquid crystal mixture were emulsified with five parts of a 1 percent, by weight, aqueous solution of gelatine having suitable film strength. Emulsified droplets of liquid crystal material ranged in size from about ten microns to about twenty microns.

The emulsion, once prepared, was coated, with the use of a draw-down applicator, onto a substrate sheet of polyethylene terephthalate to a wet-film thickness of about ten mils. The so-called film was dried in air at about 25 degrees Centigrade. The resulting film exhibited temperature response characteristics similar to those of the film in Example I., and the color producing temperature was observed to be about 70 degrees Centigrade, with 25 to 30 degrees Centigrade as the temperature range for complete spectral color change.

The dried film of this example can be stripped from its substrate and used in the same manner as the film in Example I.

Figure 1b shows the coated substrate sheet 10 of Fig.1a with the liquid crystal material 11 in the mesomorphic state. Fig.1a is intended to represent the film coating at a temperature above or below that which is required for coloration of the mesomorph - containing film material, while Fig.1b is to represent the same film coating within the temperature range of coloration. The hatching of the droplets in Fig.1b is used to depict a color change from that of Fig.1a and not to suggest particular colors, because iridescence cannot well be suggested by hatching. The coated film can be of a thickness to include only a single layer or a few layers of liquid crystal droplets, or the film can include several layers of droplets within its thickness. Droplets of liquid crystal material can range in size from about five microns to about twenty-five microns and are preferably ten to twenty microns in diameter. Depending upon conditions and requirements for use of the intended coating, several layers which include liquid crystal material of different temperature response ranges can be superimposed in direct or overlapping relation on a surface; or discrete areas of surface can be coated with layers which include different types of liquid crystal material to obtain temperature response corresponding to the coated pattern and the material coated.

Figure 2 is a diagrammatic edge view of a self-supporting film containing minute droplets 11 of a single type of liquid crystal material dispersed in a matrix of polymeric binder material 12. Although the film is depicted as having a thickness of only a few droplets diameters, in practice the film may be of any thickness extending from slightly more than one droplet diameter at its thinnest extreme up to gross dimensions of several millimeters. The optional colored layer 13 shown in this figure as well as in Figs. 1a and 1b and in Fig. 3, to follow, may be provided or not, as desired, its purpose being to color and/or opacify one surface of the film and thereby act as a background for observing the hue or to enhance the color brilliance of the display.

Figure 3 is a diagrammatic edge view of a self-supporting film containing minute droplets 11 of more than one type of liquid crystal material dispersed in a matrix of polymeric binder material 12. The figure depicts two different types of liquid crystal material contained within the film coating, a first type, for which the ambient film temperature is either above or below the temperature of its mesomorphic state, and a second type, which exists in the mesomorphic state at the film temperature of this figure. It is understood that more than just two different types of liquid crystal material may be included in a film.

Following are examples of specific embodiments of the invention ...

EXAMPLE I

In this example, a mixture of the specified liquid crystal materials was used which consisted of 55 percent, by weight, oleyl cholesteryl carbonate and

EXAMPLE TXX

In this example, one part, by weight, of the same liquid crystal mixture as was used in Example II was emulsified in five parts, by weight, of a 22 percent, by weight, aqueous solution of poly (acrylate) polymeric material. The poly (acrylate) material was ammonium poly (acrylate) and was characterized by having a pH of 8.5 to 9.5 in a 22 percent, by weight, aqueous solution and by having a viscosity of 150 to 189 250 centipoises in a 5 percent, by weight, aqueous solution. Emulsification was conducted in a jacketed Waring Blendor cup equipped with a resistance-wire heater, and the temperature of the emulsified liquid was maintained at 50 degrees Centigrade. Liquid crystal droplets in the emulsion were ten to twenty microns in diameter.

The emulsion, once prepared, was coated and dried as described in Example II, and the behavior of the dried film was noted to be essentially identical to that of

Example II with respect to color change according to change in temperature, since the liquid crystal mixture was the same in hnth example, the dried binder seemingly having little effect as to light-response. A coating was also prepared using glass as the substrate, and results were comparable to those described above.

EXAMPLE IV

This example was provided to demonstrate an embodiment of the subject invention wherein the polymeric binder material, which serves to secure droplets of liquid crystal material in dispersion in the matrix, is colored to reduce its transparency to incident light. The colored matrix-like material of this example, thereby, effectively contrasts with the iridescence of entrapped liquid crystal droplets without reliance on opaque substrates or other applied contrasting material.

Three parts, by weight, of a mixture of 85 percent, by weight, of cholesteryl nonanoate and 15 percent, by weight, oleyl cholesteryl carbonate were emulsified with five parts, by weight, of a colored binder solution, described below, in a jacketed Waring Blendor cup which w-a controlled to maintain the liquid temperature at about 50 degrees Centigrade. To prepare the binder solution, 10 grams of the poly(vinyl alcohol) specified

in Example I was dissolved in 90 millilitres of Water, and to the solution was added 10 millilitres of fountain-pen black ink,

The emulsion, having been prepared with droplets of liquid crgstnl material of about 5-25 microns in size, was coated to a wet-film thickness of ten mils onto a transparent, uncolored, sheet of polyethylene terephthalate, using a draw-down applicator as in Example I, and the coating was allowed to dry in air at about 25 degrees Centigrade. The dried emulsion film could be used either as a thin self-supporting film stripped from its substrate or together with the substrate to provide durability. Change in temperature of the film in the presence of incident light resulted in the characteristic color change, which first became evident for this mixture of liquid crystal material as the temperature rose to about 55 degrees Centigrade, iridescence being caused by a variation in temperature over the film area.

EXAMPLE V

The materials used in this example were identical with those in Example IV. In this example, however, the emulsion was sprayed onto the substrate by means of a spray gun, and the resulting dried film demonstrated color-reflecting characteristics similar to those, of Example IV.

EXAMPLE VI

In this example, the polymeric binder material was zein, a prolamine filmformer derived from the alcohol extraction of zein, a grain commonly called Indian corn. The solvent system utilized in this example was a solution of nine parts, by volume, of methanol and one part by volume of water. A solution of binder material was prepared by dissolving 80 grams of zein in 400 millilitres of the solvent system.

An emulsion was prepared in a jacketed Waring Blendor cup controlled to maintain a temperature of about 50 degrees Centigrade. The emulsion consisted of 50 millilitres of the binder material solution and 10 millilitres of a one-to-one-mixture of oleyl cholesteryl carbonate and cholesteryl nonanoate.

The emulsion was coated as in Example II, and results were similar to those of Example II with regard to iridescent effect.

EXAMPLE VII

This example demonstrates the use of an emulsion which has two different types of liquid crystal materials separately included therein. The emulsion-coating liquid system was prepared by stirring together two emulsions which have different liquid crystal materials emulsified in

separate solutions of the same kind of binder material.

The two emulsions were prepared as follows:

- a) 25 millilitres of 10 percent, by weight, aqueous poly (vinyl alcohol) was emulsified with 15 grams of a mixture of 85 percent, by weight, cholesteryl nonanoate and 15 percent by weight, oleyl cholesteryl carbonate.
- b) 25 millilitres of the 10 percent, by weight, aqueous poly(vinyl alcohol) was emulsified with 15 grams of a mixture of 85 percent, by weight, cholesteryl nonanoate and 15 percent, by weight, oleyl cholesteryl carbonate.

The two emulsions were then stored together carefully and by hand, it being discovered that undue agitation in combining these particular emulsions causes mixing together of the droplets of liquid crystal material.

The emulsion coating system with two different liquid crystal materials was coated onto a substrate and dried in the air at about 25 degrees Centigrade.

The visual effect of a coated dried emulsion of this example was much the same as that of the previous examples, except that color change appeared in the coating in two sequences beginning at two different temperatures. As a comparison to the visual effect described in Example I., for a coating having only one liquid crystal material, the

following describes a coating with two liquid crystal materials...

In warming a test point on the film a first sequence of concentric rings of color appeared, circling the point of heat application. When the point on the film was further warmed above the first color producing temperature but below the color producing temperature of the second emulsified material, the test point again appeared uncolored, with only a ring of color remaining, at that time, a fixed distance from the centre of the heat source, due to the static temperature gradient. Upon further warming of the test point on the film, a second set of color rings began to appear and move outwardly, but never reached the outwardly moving first ring, giving rise to a visual indication of two temperature ranges at different locations on the coated substrate. So much for point application of heat. When the coated substrate, as a whole, was heated, the film reflected changing color not in rings, but all over, colors first appearing due to the liquid crystal material and then, on further heating, the film appearing uncolored, due to the second liquid crystal material, for a time at temperatures intermediate to the different color producing temperatures. The color changes appeared in reverse order on cooling of the film.

Where, in A given small area, there are present two kinds of the, liquid drops which exhibit different color reflectance at a given temperature, the effect on the eye is additive, as would be expected.