

[54] **LIQUID CRYSTAL THERMAL IMAGING SYSTEM HAVING AN UNDISTURBED IMAGE ON A DISTURBED BACKGROUND**

[72] Inventors: **Bela Mechlowitz**, Rochester; **James E. Adams**, Ontario; **Werner Erwin Louis Haas**, Webster, all of N.Y.

[73] Assignee: **Xerox Corporation**, Stamford, Conn.

[22] Filed: **Jan. 6, 1971**

[21] Appl. No.: **104,348**

[52] U.S. Cl. **250/83 R, 250/65 R, 250/83.3 HP, 252/408, 350/157, 350/160 LC**

[51] Int. Cl. **G02f 1/16**

[58] Field of Search. **250/65 R, 83 R, 83 CD, 83.3 H, 250/83.3 HP; 350/160, 157; 252/408**

[56] **References Cited**

UNITED STATES PATENTS

3,114,836 12/1963 Fergason et al. 250/83 R
3,401,262 9/1968 Fergason et al. 250/83 R

3,415,991 12/1968 Asars 250/83 R
3,529,156 9/1970 Fergason et al. 250/83 R
3,569,709 3/1971 Wank 250/83 R X
3,604,930 9/1971 Allen 250/83 R

Primary Examiner—Ronald L. Wibert

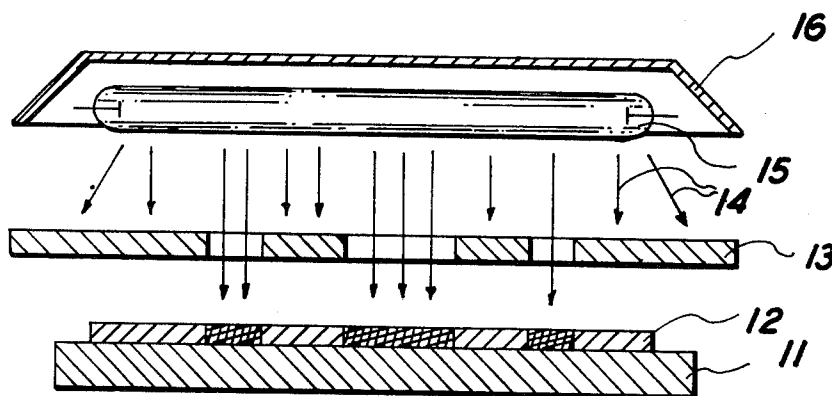
Assistant Examiner—Edward S. Bauer

Attorney—James J. Ralabate, David C. Petre and Roger W. Parkhurst

[57] **ABSTRACT**

An imaging system wherein an imaging member comprising a material having a cholesteric liquid crystalline phase in its Grandjean or "disturbed" texture state is thermally imaged by imagewise heating image portions of said imaging material to a temperature at least about the cholesteric liquid crystalline-liquid isotropic transition temperature of said material and allowing said heated portions of said imaging material to return to a temperature within the cholesteric liquid crystalline mesophase temperature range of said material whereby said imaged areas assume the focal-conic or "undisturbed" texture state in the desired image configuration. Images provided by the inventive system are erasable, and the imaging members are reusable.

20 Claims, 4 Drawing Figures



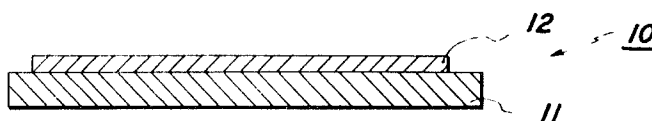


FIG. 1

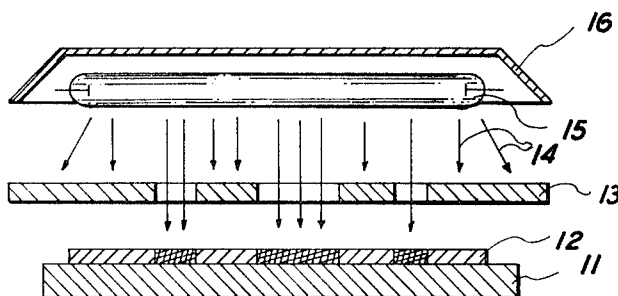


FIG. 2

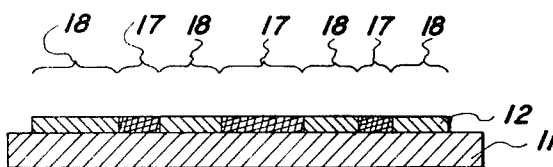


FIG. 3

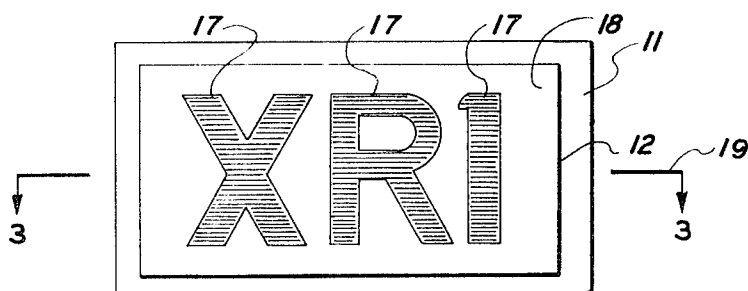


FIG. 4

INVENTORS,
BELA MECHLOWITZ
JAMES E. ADAMS
BY WERNER E.L. HAAS

Rogers Parkhurst
ATTORNEY

LIQUID CRYSTAL THERMAL IMAGING SYSTEM HAVING AN UNDISTURBED IMAGE ON A DISTURBED BACKGROUND

BACKGROUND OF THE INVENTION

This invention relates to imaging systems, and more specifically, to an imaging system herein the imaging member comprises an imaging material having colesteric liquid crystalline characteristics. Furthermore, this invention more specifically relates to a novel system of thermally imaging such a liquid crystalline imaging member.

Recently there has been substantial interest in the discovery of more useful applications for the class of substances known as "liquid crystals." The name "liquid crystals" has become generic to liquid crystalline materials which exhibit dual physical characteristics, some of which are typically associated with liquids and others which are typically unique to solids. Liquid crystals exhibit mechanical characteristics, such as viscosities, which are ordinarily associated with liquids. The optical scattering and transmission characteristics of liquid crystals are similar to those characteristics ordinarily unique to solids. In liquids or fluids, the molecules are typically randomly distributed and oriented throughout the mass of the substance. Conversely, in crystalline solids the molecules are generally rigidly oriented and arranged in a specific crystalline structure. Liquid crystals resemble solid crystals in that the molecules of the liquid crystalline substances are regularly oriented in a fashion analogous to but less extensive than the molecular orientation and structure in a crystalline solid. Many substances have been found to exhibit liquid crystalline characteristics in a relatively narrow temperature range; but below such temperature ranges the substances typically appear as crystalline solids and above such temperature ranges they typically appear as liquids. Liquid crystals are known to appear in three different mesomorphic forms: smectic, nematic, and colesteric. In each of these structures the molecules are typically arranged in a specific, unique orientation.

Liquid crystals have been found to be sensitive or responsive to a variety of stimuli including temperature, pressure, foreign chemical compounds, and electric and magnetic fields, as disclosed, for example, in copending application Ser. No. 646,532, filed June 16, 1967; copending application Ser. No. 4,644, filed Jan. 21, 1970; French Pat. No. 1,484,584; Ferguson U.S. Pat. No. 3,409,404; and Waterman et al U.S. Patent No. 3,439,525. In particular, various temperature effects on liquid crystals are described in Ferguson et al U.S. Pat. Nos. 3,114,836, Ferguson 3,410,999, Asars 3,415,991, and Woodmansee 3,441,513.

Most recently, imaging systems wherein the imaging member comprises a liquid crystalline material have been discovered, and are described, for example, in copending application Ser. No. 821,565, filed May 5, 1969; Ser. No. 849,418, filed Aug. 12, 1969; and Ser. No. 867,593, filed Oct. 20, 1969.

Colesteric liquid crystals are known to exhibit various observable textures. For example, colesteric liquid crystals may adopt a homeotropic, a focal-conic, or a Grandjean plane texture as modifications of the colesteric mesophase itself, as described, for example, in Gray G.W., *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London, 1962, pp. 39-54. An imaging system making use of these different textures is described in application Ser. No. 867,593.

In new and growing areas of technology such as liquid crystalline imaging systems, new methods, apparatus, compositions, and articles of manufacture are often discovered for the application of the new technology and a new mode. The present invention relates to a new and advantageous system for imaging colesteric liquid crystalline members.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a novel imaging system.

It is another object of this invention to provide a novel liquid crystal imaging system.

It is another object of this invention to provide an imaging system which produces high resolution images from thermal stimuli.

It is another object of this invention to provide an imaging or display system having an image memory capacity.

It is another object of this invention to provide an erasible image or display and reuseable imaging members.

It is another object of this invention to provide an imaging system which requires no development step nor a pretreating step such as electrically charging or chemically activating.

It is another object of this invention to provide an imaging system suitable for use in display devices which may be addressed by thermal means or other suitable means.

It is yet another object of this invention to provide a color display and imaging system.

The foregoing objects and others are accomplished in accordance with this invention by a system wherein an imaging member comprising a material having a colesteric liquid crystalline phase in its Grandjean or "disturbed" texture state is thermally imaged by imagewise heating image portions of said imaging material to a temperature above the colesteric liquid crystalline mesomorphic state temperature range of said material and allowing said heated portions of said imaging material to return to a temperature within the colesteric liquid crystalline mesophase temperature range of said material whereby said imaged areas assume the focal-conic or "undisturbed" texture state in the desired image configuration. Images provided by this inventive system are erasible, and the imaging members are reuseable.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the invention as well as other objects and further features thereof, reference is made to the following detailed disclosure of the preferred embodiments of the invention taken in conjunction with the accompanying drawings thereof, wherein:

FIG. 1 illustrates in partially schematic, cross-sectional view, an imaging member suitable for use in the present invention.

FIG. 2 illustrates in partially schematic, cross-sectional view, an imaging member being imaged by the inventive imaging system.

FIG. 3 illustrates in partially schematic, cross-sectional view, an imaging member which has been imaged by the inventive system.

FIG. 4 is a view of the face of the imaged member of FIG. 3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In FIG. 1 an imaging member 10 suitable for use in the advantageous system of the present invention is illustrated wherein substrate 11 supports a layer of imaging composition comprising material which exhibits a colesteric liquid crystalline mesophase.

The supporting substrate 11 may comprise any suitable material, and in various embodiments, the substrate may take on any suitable form including the form of a web, foil, laminate or the like, strip, sheet, coil, cylinder, drum, endless belt, endless moebius strip, circular disc or other geometrical shapes. The substrate material may be transparent, translucent, or opaque. In particularly preferred embodiments of the imaging members of the present invention, the substrate is preferably a material which exhibits low thermal conductivity. Of course, the substrate material should be compatible with the material comprising the layer of imaging composition 12.

The layer of imaging composition 12 may comprise any suitable material which exhibits the colesteric liquid crystalline mesophase.

Any suitable colesteric liquid crystal, mixture or composition comprising liquid crystals, or composition having colesteric liquid crystalline characteristics may be used

therein. Cholesteric liquid crystals suitable for use in the present invention include derivatives from reactions of cholesterol and inorganic acids; for example, cholesteryl chloride, cholesteryl bromide, cholesteryl iodide, cholesteryl fluoride, cholesteryl nitrate; esters derived from reactions of cholesterol and carboxylic acids; for example, cholesteryl crotonate; cholesteryl nonanoate, cholesteryl hexanoate; cholesteryl formate; cholesteryl docosanoate; cholesteryl chloroformate; cholesteryl propionate; cholesteryl acetate; cholesteryl valerate; cholesteryl vacconate; cholesteryl linoleate; cholesteryl linolenate; cholesteryl oleate; cholesteryl erucate; cholesteryl butyrate; cholesteryl caprate; cholesteryl laurate; cholesteryl myristate; cholesteryl clupanodionate; ethers of cholesterol such as cholesteryl decyl ether; cholesteryl lauryl ether; cholesteryl oleyl ether; cholesteryl dodecyl ether; carbamates and carbonates of cholesterol such as cholesteryl decyl carbonate; cholesteryl oleyl carbonate; cholesteryl methyl carbonate; cholesteryl ethyl carbonate; cholesteryl butyl carbonate; cholesteryl docosonyl carbonate; cholesteryl cetyl carbonate; cholesteryl-p-nonylphenyl carbonate; cholesteryl-2-(2-ethoxyethoxy)ethyl carbonate; cholesteryl-2-(2-Butoxyethoxy)ethyl carbonate; cholesteryl-2-(2-methoxyethoxy)ethyl carbonate; cholesteryl heptyl carbamate; and alkyl amides and aliphatic secondary amines derived from 3 β -amino- Δ 5-cholestene and mixtures thereof; peptides such as poly- γ -benzyl-L-glutamate; derivatives of beta sitosterol such as sitosteryl chloride; and active amyl ester of cyanobenzylidene amino cinnamate. The alkyl groups in said compounds are typically saturated or unsaturated fatty acids, or alcohols, having less than about 25 carbon atoms, and unsaturated chains of less than about 5 double-bonded olefinic groups. Aryl groups in the above compounds typically comprise simply substituted benzene ring compounds. Any of the above compounds and mixtures thereof may be suitable cholesteric liquid crystalline materials in the advantageous system of the present invention.

Smectic liquid crystalline materials are suitable for use as components of the imaging composition in the present invention and such smectic liquid crystal materials include: n-propyl-4'-ethoxy biphenyl-4-carboxylate; 5-chloro-6-n-heptyloxy-2-naphthoic acid; lower temperature mesophases of cholesteryl octanoate, cholesteryl nonanoate, and other open-chain aliphatic esters of cholesterol with chain length of 7 or greater; cholesteryl oleate; sitosteryl oleate; cholesteryl decanoate; cholesteryl laurate; cholesteryl myristate; cholesteryl palmitate; cholesteryl stearate; 4'-n-alkoxy-3'-nitrobiphenyl-4-carboxylic acids' ethyl-p-azoxy-cinnamate; ethyl-p-4-ethoxybenzylideneaminocinnamate; ethyl-p-azoxybenzoate; potassium oleate; ammonium oleate; p-n-octyloxybenzoic acid; the low temperature mesophase of 2-p-n-alkoxybenzylideneamino-fluorenones with chain length of 7 or greater; the low temperature mesophase of p-(n-heptyl)oxybenzoic acid; anhydrous sodium stearate; thallium (I) stearate; mixtures thereof and others.

Nematic liquid crystalline materials suitable for use as components of the imaging composition in the advantageous system of the present invention include: p-azoxyanisole, p-azoxyphenetole, p-butoxybenzoic acid, p-methoxy-cinnamic acid, butyl-p-anisylidene-p-aminocinnamate, anisylidene para-amino-phenylacetate, p-ethoxy-benzalamino-a-methyl-cinnamic acid, 1,4-bis(p-ethoxy benzylidene) cyclohexanone, 4,4'-dihexyloxybenzene, 4,4'-diheptyloxybenzene, anisal-p-amino-azo-benzene, anisaldazine, a-benzeneazo- (anisal- α' -naphthylamine), n,n'-nonoxybenzetoluidine; anils of the generic group (p-n-alkoxybenzylidene-p-n-alkylanilines), such as methoxy benzylidene butylaniline, mixtures of the above and many others.

The above lists of materials exhibiting various liquid crystalline phases are not intended to be exhaustive or limiting. The lists disclose a variety of representative materials suitable for use in the imaging composition or mixture comprising cholesteric liquid crystalline materials, which comprises the active imaging element in the advantageous system of the present invention.

The liquid crystalline materials may be prepared by dissolving the liquid crystals or mixtures thereof in any suitable solvent, for example organic solvents such as chloroform, trichloroethylene, tetrachloroethylene, petroleum ether, methyl-ethyl ketone, and others. The solution containing the liquid crystal material is then typically poured, sprayed or otherwise applied to a suitable substrate. After evaporation of the solvent, a thin layer of liquid crystal remains. Alternatively, the individual liquid crystal materials of the liquid crystalline mixture can be combined, and applied directly by heating the mixed components above the isotropic transition temperature and mixing the components before application to a suitable substrate.

The liquid crystal imaging layers or films suitable for use in the present invention are preferably of a thickness in the range of about 250 microns or less, although thicker films will perform satisfactorily in the inventive system. Optimum results are typically achieved using layers in the thickness range between about 1 micron and about 50 microns. When a layer of imaging composition 12 is prepared on a suitable substrate 11 by methods such as those described above, the material comprising the cholesteric liquid crystalline mesophase often assumes its Grandjean or "disturbed" texture state. However, in some instances the material may be made to assume its Grandjean texture state by mechanical disturbance such as by shearing or pressure, or by external forces such as electrical or magnetic fields, or by any other suitable means. The Grandjean texture is typically characterized by selective reflection of incident light around a wavelength λ_0 where $\lambda_0 = 2np$ where n equals the index of refraction of the composition layer and p equals the pitch of the liquid crystalline film, and is additionally characterized by optical activity for wavelengths of incident light away from λ_0 . If λ_0 is in the visible spectrum the composition layer comprising cholesteric liquid crystalline material appears to have the color corresponding to λ_0 for normally incident light and observation, and if λ_0 is outside the visible spectrum the composition layer typically appears colorless and non-scattering. The Grandjean texture of cholesteric liquid crystals is sometimes referred to as the "disturbed" texture.

An imaging member 10 which is prepared so that the composition layer comprising material in the cholesteric liquid crystalline mesophase is in its Grandjean or "disturbed" texture state is imaged in the advantageous system of the present invention by the imagewise application of thermal energy or energy which is capable of producing an imagewise thermal effect in the layer of imaging composition. One embodiment of the advantageous system of the present invention is illustrated, for example, in FIG. 2 wherein the imaging composition layer 12 is shown being imagewise exposed through a stencil-like mask 13 to thermal radiation 14 which is emitted by a source 15 under shield 16. Any source of thermal energy, for example such as lasers, gas discharge lamps, and others, may be used as the source of energy in the imagewise exposure step. Furthermore, in addition to the imagewise mask or stencil exposure system described above, any suitable means of providing an imagewise exposure may be used. Even light pencils or thermal styli are suitable for use in various embodiments.

In the inventive system the thermal energy which is applied in imagewise configuration to the layer of imaging composition is applied in sufficient amounts so that the imaging composition comprising material having the cholesteric liquid crystalline mesophase is, in the imagewise exposed areas, heated to a temperature at least about the liquid crystalline-liquid isotropic transition temperature of the imaging material having the cholesteric liquid crystalline mesophase characteristics. After the imagewise application of sufficient thermal energy to raise the temperature of the imaging composition in the imagewise exposed areas to a temperature at least about the isotropic transition temperature, the source of thermal energy is removed, and the imaging composition is allowed to cool into the cholesteric liquid crystalline mesophase temperature range below the isotropic transition temperature of the composition.

While in many embodiments, the temperature is typically raised to or above the liquid isotropic transition temperature, it is found that in some embodiments temperatures within a few degrees C. of the liquid isotropic transition temperature of the imaging composition, i.e. at least about the liquid isotropic transition temperature, are sufficient to cause the desired effect in the desired image areas. For example, temperatures within about 5° C. of the isotropic transition temperature have been found sufficient to cause the desired effect in some embodiments.

Upon cooling into the cholesteric liquid crystalline mesophase temperature range, the imagewise exposed areas of the imaging composition typically exhibit the focal-conic or "undisturbed" texture state, thereby providing an imaged member having image areas of the imaging composition comprising a material having the cholesteric liquid crystalline mesophase in the focal-conic texture state with background areas of the imaging composition comprising material having a cholesteric liquid crystalline mesophase in the Grandjean type texture state.

The focal-conic type texture is also typically characterized by selective reflection; but in addition, this texture state also exhibits diffuse scattering in the visible spectrum, whether λ_0 is in the visible spectrum or not. The appearance of the focal-conic texture state is typically milky-white when λ_0 is outside the visible spectrum. The focal-conic texture of cholesteric liquid crystalline materials is sometimes referred to as the "undisturbed" texture state.

In various embodiments of the imaging member of the present invention it may be advantageous to use substrate materials which are translucent or substantially transparent to visible light. In such embodiments, the imaging member may be suitable for use as an image transparency. When the imaging composition comprising a material having a cholesteric liquid crystalline mesophase is initially prepared on the substrate, the composition typically appears colored, or colorless if transparent. If such a transparency is viewed between polarizers, the member typically appears colored or black. However, after imaging by the advantageous system of the present invention, the image areas of the composition, which have been processed by the thermally induced texture transition imaging system of the present invention, are typically observable because the composition layer becomes white in the imaged areas which diffusely scatter the polarized light which may then be transmitted, at least in part, through the polarizer to the eye of the observer. In this way, when such a transparency is observed between polarizers, the imaging system typically produces a white or light image on a dark or colored background.

The effect of thermally induced texture change in the imaged areas is to destroy polarization of transmitted light in the image areas whereas the background areas have little effect on polarization except in some small wavelength region. This small region, here designated $\Delta\lambda$, is centered about $\lambda_0 = 2np$ where n equals the index of refraction of the composition layer and p is the pitch of the cholesteric liquid crystalline material. Typically the ratio $\lambda_0/\Delta\lambda$ equals about 14. In this region, incident plane polarized light emerges from the composition layer comprising material having the cholesteric liquid crystalline mesophase, circularly polarized. Between crossed polarizers, therefore, the imaged areas typically appear white or light upon the black or colored background. Where an imaging member including a supporting substrate is viewed between crossed polarizers, the substrate material should be optically isotropic, i.e., it should not change the polarization of the light transmitted through the system.

FIG. 3 illustrates in partially schematic, cross-sectional view, an imaged member wherein the layer of imaging composition 12 exhibits imaged areas 17 in the focal-conic or "undisturbed" cholesteric liquid crystalline texture state, while the background areas 18 exhibit the Grandjean or "disturbed" cholesteric liquid crystalline texture state. The thermally induced texture transition imaging effect of the present invention is typically a bulk effect. The bulk effect is

illustrated in FIG. 3 where imaged areas 17 of the layer of imaging composition 12 are schematically illustrated as being transformed throughout the entire cross-section of the composition.

FIG. 4 is a top view of the imaging member of FIG. 3 (wherein the view of FIG. 3 is a cross-section along line 19) schematically showing imaged areas 17, in the focal-conic texture state on background areas 18, in the Grandjean texture state. Although the imaged areas 17 in FIG. 4 are here illustrated as being the darker areas, the contrast and density of an imaged member produced by the advantageous system of the present invention, may vary from one embodiment to another. FIG. 4 is intended to be a representation of an imaged member wherein the imaged areas 17 are clearly optically distinguishable from the background areas 18.

In addition to the methods of viewing images produced by the inventive system already described above, any other suitable means for viewing such images, for example in either transmitted or reflective light or even with projection devices, may be suitable for use in conjunction with the present invention. In transmitted light, imaged members (which will typically have a substantially transparent supporting substrate) will typically appear milky or white in the texture transformed imaged areas, while the untransformed background areas of the layer of imaging composition will typically remain more light transmissive or translucent. The transmitted light mode of observing such images is particularly suited for use in image projection systems which typically magnify the size of the image produced by the inventive system. When viewed in reflected light, the imaged member exhibits clearly distinguishable image and background areas which may be of different colors or have colored image areas on a substantially colorless background. For example, in one specific mode, an infra-red reflective (i.e., transparent) layer of imaging composition is provided on a mirror substrate and imaged to convert the imagewise transformed areas into the visible focal-conic texture, thereby providing colored image areas on a substantially transparent background through which incident light is reflected by the mirror substrate.

In addition to the imaging aspects of the inventive system, it should also be noted that the imaging members of the present invention may have images like those produced by the inventive system erased, for example by the application of external forces such as pressure, shearing stresses, electrical fields, magnetic fields, or combinations thereof. These erasure methods are essentially the same methods which were discussed earlier herein as methods by which the imaging composition may be made to assume its Grandjean or "disturbed" texture state. After such an imaged member has the image erased, the member is typically suitable for re-imaging by the inventive system. In this way, imaging members of the present invention are reusable for large numbers of imaging and erasing cycles. The erasability of the inventive system further enhances the utility of this one-step, immediately visible imaging system.

In many embodiments of imaging members suitable for use in the inventive system, it may be highly desirable to have the layer of imaging composition overcoated with or encapsulated in a thin transparent overcoating material. For example, a layer of cholesteric imaging composition on a suitable substrate may be overcoated with a thin, transparent sheet of Mylar polyester resin film, available from DuPont; transparent polyethylene, polyvinyl chloride, or Tedlar, a polyvinyl-fluoride resin film available from DuPont; or thin glass overcoatings. Alternately, the layer of imaging composition may be encapsulated between two layers of the overcoating film.

Such overcoating or encapsulating films are typically not greater than about 10 mils thick, with thinner films being preferred. The films are transparent, preferably not infra-red absorbing, preferably not of high heat capacity, and otherwise compatible with the other elements of the imaging system.

Although the inventive system has been generically described above in conjunction with the drawings FIG. 1 -

FIG. 4, any suitable means or materials which may combine to effect the desirable result of the inventive system may be used in the various process steps of the inventive system. The means for applying thermal energy in imagewise configuration to the imaging member may comprise any suitable means. For example, as illustrated in FIG. 2, any suitable heating means 15 may be used to project thermal energy 14 through any suitable masking element 13. Similarly, any suitable source of thermal energy, said source itself being in imagewise configuration, may be used. For example, a heated stylus, or other heated member itself in the desired imagewise configuration, may be brought into close proximity with the imaging composition layer to produce the advantageous results of the inventive system. A particularly preferred method of thermally imaging in the inventive system comprises briefly flashing a high energy Xenon flash lamp over an imaging member which is optically masked in the desired image configuration. Other sources of the desired thermal energy may include modulated lasers or light styli. In still other systems where the imaging composition is used in conjunction with electrically conductive substrates or masks, RF microwave energy inputs may be used to imagewise expose the composition to thermal energy to produce the inventive effects.

The imagewise exposed areas of the imaging composition in the inventive system are subjected to energy inputs which are typically in the range between about 1 and about 100 millijoules/cm² of imaging surface area, depending upon the thickness of the imaging composition and the proximity of the imaging transition temperature to the initial temperature of the imaging member. It is again noted that the inventive imaging system produces a bulk effect in the layer of imaging composition. It has been found that the short duration, high intensity flash imaging mode of the present invention is particularly advantageous because of its speed, which limits the time in which lateral thermal conductivity can take place and thereby increases resolution in the inventive imaging system. Of course, prudent selection of imaging compositions and substrates helps inhibit the lateral thermal conductivity and thereby correspondingly enhances resolution in the inventive system.

A clear understanding of the novel texture transition imaging system of the present invention makes it clear that the temperature conditions under which the system is to be used may make some imaging compositions preferred for use under certain conditions. For example, when the present imaging system is used at room temperature, imaging compositions which exhibit cholesteric liquid crystalline characteristics at or near room temperature (i.e. in the range between about 20° C. and about 30° C.) are preferred. In addition it is usually preferable to use imaging compositions whose cholesteric liquid crystalline mesophase-liquid isotropic transition temperature is significantly above the surrounding conditions under which the system is to be used; such compositions minimize thermal destruction or erasure of the desired image.

The following examples further specifically define the present invention with respect to the thermally induced imagewise transformation of image portions of a layer of imaging composition comprising a material having cholesteric liquid crystalline characteristics, from the Grandjean or "disturbed" texture to an imaged, focal-conic or "undisturbed" texture. The parts and percentages are by weight unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of the novel liquid crystal imaging system.

EXAMPLE I

An imaging member is provided by dissolving a solute mixture comprising about 57 percent cholesteryl formate and about 43 percent cholesteryl nonanoate in petroleum ether solvent, mixing the solution thoroughly, and depositing a layer of the solution on a thick, stable black plastic substrate. The solvent is allowed to evaporate, leaving a layer of imaging

composition comprising cholesteric liquid crystalline materials in a thickness of about 12 microns on the substrate. After solvent evaporation, the film of imaging composition is uniformly provided in the Grandjean texture state by shearing the film by dragging the edge of a glass slide across the surface of the film. The film exhibits a green color. The imaging member is then imaged by the texture transition imaging system by placing the member, imaging composition side up, spaced a few microns under an imagewise metal mask, and placing the masked member about 25 cm from a BH6-1 mercury arc lamp. The lamp is activated thereby exposing the member through the mask for an exposure time of about 10 seconds. The imagewise exposure heats the image areas to temperatures about or above the cholesteric liquid crystalline-liquid isotropic transition temperature of the imaging composition, and the imaged areas exhibit a texture transition. A clearly optically distinguishable image, corresponding to the mask, of almost colorless imaged areas on a green colored background, appears almost immediately upon exposure. The composition is allowed to cool into its cholesteric liquid crystalline mesophase temperature range.

The imaged areas exhibit the focal-conic or "undisturbed" texture state while the background areas of the cholesteric liquid crystalline imaging composition exhibit the Grandjean or "disturbed" texture state.

EXAMPLE II

An imaged member is provided by the method of Example I. After imaging, this imaged member is covered with a transparent glass slide. The glass slide is slightly displaced with respect to the substrate of the imaged member. Displacing the cover slide erases the texture transformed image and uniformly provides the cholesteric liquid crystalline imaging composition in the Grandjean texture state.

EXAMPLE III

An imaging member is provided by mixing about 57 percent cholesteryl formate and about 43 percent cholesteryl nonanoate, placing the mixture in a crucible, and heating the mixture above the liquid isotropic transition temperature of the mixture and its components. The liquid mixture is thoroughly mixed in the crucible while the composition is in the liquid state. The liquid composition is applied to a transparent glass substrate, and squeezed into a substantially uniform layer of imaging composition of a thickness of about 19 microns. The composition is allowed to cool into its cholesteric liquid crystalline mesophase temperature range, and the member is imaged as described in Example I.

The imaged member is examined under a microscope, and the image areas are seen to exhibit the focal-conic or "undisturbed" texture state, and are colorless, while the background areas are seen to exhibit a green color and are in the Grandjean or "disturbed" texture state.

EXAMPLE IV

An imaged member is provided by the method of Example III. After imaging the imaged member is covered with a transparent glass slide. Pressure is applied throughout the area of the slide, thereby erasing the texture transformed image and uniformly providing the cholesteric liquid crystalline imaging composition in the Grandjean texture state.

EXAMPLES V - VII

Imaging members are provided as described in Example I, except that the solute mixture comprises:

- V About 30 percent cholesteryl formate and about 70 percent cholesteryl nonanoate;
- VI About 70 percent cholesteryl formate and about 30 percent cholesteryl nonanoate;
- VII About 76 percent cholesteryl formate and about 24 percent cholesteryl nonanoate.

The imaging members are imaged as described in Example I, resulting in clearly optically distinguishable images. The imaged members are erased by the method described in Example II.

EXAMPLES VIII - LXXIX

Imaging members are provided as described in Example III, except that the imaging composition having cholesteric liquid crystalline characteristics comprises:

- VIII About 74 percent cholesteryl chloride and about 26 percent cholesteryl acetate;
- IX About 68 percent cholesteryl chloride and about 32 percent cholesteryl acetate;
- X About 60 percent cholesteryl chloride and about 40 percent cholesteryl acetate;
- XI 90 percent cholesteryl chloride and about 10 percent cholesteryl laurate;
- XII About 82 percent cholesteryl chloride and about 18 percent cholesteryl laurate;
- XIII About 76 percent cholesteryl chloride and about 24 percent cholesteryl laurate;
- XIV About 93 percent cholesteryl chloride and about 7 percent cholesteryl propionate;
- XV About 89 percent cholesteryl chloride and about 11 percent cholesteryl propionate;
- XVI About 80 percent cholesteryl chloride and about 20 percent cholesteryl hexanoate;
- XVII About 70 percent cholesteryl chloride and about 30 percent cholesteryl hexanoate;
- XVIII About 91 percent cholesteryl chloride and about 9 percent cholesteryl stearate;
- XIX About 87 percent cholesteryl chloride and about 13 percent cholesteryl stearate;
- XX About 79 percent cholesteryl chloride and about 21 percent cholesteryl stearate;
- XXI About 84 percent cholesteryl chloride and about 16 percent cholesteryl myristate;
- XXII About 78 percent cholesteryl chloride and about 22 percent cholesteryl myristate;
- XXIII About 10 percent cholesteryl chloride and about 90 percent cholesteryl oleyl carbonate;
- XXIV About 20 percent cholesteryl chloride and about 80 percent cholesteryl oleyl carbonate;
- XXV About 30 percent cholesteryl chloride and about 70 percent cholesteryl oleyl carbonate;
- XXVI About 40 percent cholesteryl chloride and about 60 percent cholesteryl oleyl carbonate;
- XXVII About 66 percent cholesteryl chloride and about 34 percent cholesteryl oleyl carbonate;
- XXVIII About 71 percent cholesteryl chloride and about 29 percent cholesteryl oleyl carbonate;
- XXIX About 80 percent cholesteryl chloride and about 20 percent cholesteryl oleyl carbonate;
- XXX About 90 percent cholesteryl chloride and about 10 percent cholesteryl oleyl carbonate;
- XXXI About 88 percent cholesteryl chloride and about 12 percent cholesteryl caprylate;
- XXXII About 80 percent cholesteryl chloride and about 20 percent cholesteryl caprylate;
- XXXIII About 80 percent cholesteryl chloride and about 20 percent cholesteryl iodide;
- XXXIV About 50 percent cholesteryl chloride and about 50 percent cholesteryl iodide;
- XXXV About 20 percent cholesteryl chloride and about 80 percent cholesteryl iodide;
- XXXVI About 80 percent cholesteryl chloride and about 20 percent cholesteryl 2(2-butoxy ethoxy) ethyl carbonate;
- XXXVII About 70 percent cholesteryl chloride and about 30 percent cholesteryl 2(2-butoxy ethoxy) ethyl carbonate;

- XXXVIII About 40 percent cholesteryl chloride and about 60 percent cholesteryl 2(2-butoxy ethoxy) ethyl carbonate;
- XXXIX About 30 percent cholesteryl chloride and about 70 percent cholesteryl 2(2-butoxy ethoxy) ethyl carbonate;
- XL About 30 percent cholesteryl chloride and about 70 percent cholesteryl nonanoate;
- XLI About 42 percent cholesteryl chloride and about 58 percent cholesteryl nonanoate;
- XLII About 49 percent cholesteryl chloride and about 51 percent cholesteryl nonanoate;
- XLIII About 54 percent cholesteryl chloride and about 46 percent cholesteryl nonanoate;
- XLIV About 75 percent cholesteryl chloride and about 25 percent cholesteryl nonanoate;
- XLV About 80 percent cholesteryl chloride and about 20 percent cholesteryl nonanoate;
- XLVI About 90 percent cholesteryl chloride and about 10 percent cholesteryl nonanoate;
- XLVII About 72 percent cholesteryl chloride and about 28 percent cholesteryl heptanoate;
- XLVIII About 80 percent cholesteryl chloride and about 20 percent cholesteryl heptanoate;
- XLIX About 86 percent cholesteryl chloride and about 14 percent cholesteryl heptanoate
- L About 10 percent cholesteryl chloride and about 90 percent cholesteryl bromide
- LI About 20 percent cholesteryl chloride and about 80 percent cholesteryl bromide
- LII About 30 percent cholesteryl chloride and about 70 percent cholesteryl bromide
- LIII About 50 percent cholesteryl chloride and about 50 percent cholesteryl bromide
- LIV About 66 percent cholesteryl chloride and about 34 percent cholesteryl butyrate;
- LV About 74 percent cholesteryl chloride and about 26 percent cholesteryl butyrate;
- LVI About 80 percent cholesteryl chloride and about 20 percent cholesteryl butyrate;
- LVII About 73 percent cholesteryl chloride and about 27 percent cholesteryl caproate;
- LVIII About 83 percent cholesteryl chloride and about 17 percent cholesteryl caproate;
- LIX About 89 percent cholesteryl chloride and about 11 percent cholesteryl caproate;
- LX About 80 percent cholesteryl chloride and about 20 percent cholesterol;
- LXI About 90 percent cholesteryl chloride and about 10 percent cholesterol;
- LXII About 68 percent cholesteryl chloride and about 32 percent cholesteryl valerate;
- LXIII About 74 percent cholesteryl chloride and about 26 percent cholesteryl valerate;
- LXIV About 84 percent cholesteryl chloride and about 16 percent cholesteryl valerate;
- LXV About 55 percent cholesteryl chloride and about 45 percent cholesteryl 2(2-ethoxy-ethoxy) ethyl carbonate;
- LXVI About 20 percent cholesteryl chloride and about 80 percent cholesteryl 2(20ethoxy-ethoxy) ethyl carbonate;
- LXVII About 10 percent cholesteryl chloride and about 90 percent cholesteryl 2(2-ethoxy-ethoxy) ethyl carbonate;
- LXVIII About 50 percent cholesteryl n-propyl carbonate and about 50 percent cholesteryl 2(2-ethoxy-ethoxy) ethyl carbonate;
- LXIX About 68 percent cholesteryl n-propyl carbonate and about 32 percent cholesteryl 2(2-ethoxy-ethoxy) ethyl carbonate;
- LXX About 20 percent cholesteryl n-propyl carbonate and about 80 percent cholesteryl 2(2-butoxy ethoxy) ethyl carbonate;
- LXXI About 15 percent cholesteryl oleyl carbonate and about 85 percent anisylidene-p-n-butylaniline, (hereafter ABUTA);

- LXXII About 20 percent cholesteryl oleyl carbonate and about 80 percent ABUTA;
- LXXIII About 27 percent cholesteryl oleyl carbonate and about 73 percent ABUTA;
- LXXIV About 35 percent cholesteryl oleyl carbonate and about 65 percent ABUTA;
- LXXV About 80 percent cholesteryl oleyl carbonate and about 20 percent ABUTA
- LXXVI About 80 percent cholesteryl oleyl carbonate and about 20 percent cholesterol;
- LXXVII About 90 percent cholesteryl oleyl carbonate and about 10 percent cholesterol;
- LXXVIII About 10 percent cholesterol and about 45 percent cholesteryl oleyl carbonate and about 45 percent cholesteryl 2(2-ethoxy-ethoxy) ethyl carbonate;
- LXXIX About 20 percent cholesterol and about 40 percent cholesteryl oleyl carbonate and about 40 percent cholesteryl 2(2-ethoxy-ethoxy) ethyl carbonate;
- LXXX About 10 percent cholesterol and about 45 percent cholesteryl oleyl carbonate and about 45 percent cholesteryl chloride;
- LXXXI About 20 percent cholesterol and about 40 percent cholesteryl oleyl carbonate and about 40 percent cholesteryl chloride;
- LXXXII About 72 percent cholesteryl chloride and about 14 percent cholesteryl propionate and about 14 percent cholesteryl decanoate;
- LXXXIII About 76 percent cholesteryl chloride and about 12 percent cholesteryl propionate and about 12 percent cholesteryl decanoate;
- LXXXIV About 80 percent cholesteryl chloride and about 10 percent cholesteryl propionate and about 10 percent cholesteryl decanoate;
- LXXXV About 84 percent cholesteryl chloride and about 8 percent cholesteryl propionate and about 8 percent cholesteryl decanoate;
- LXXXVI About 88 percent cholesteryl chloride and about 6 percent cholesteryl propionate and about 6 percent cholesteryl decanoate;
- LXXXVII About 38 percent cholesteryl chloride and about 38 percent cholesteryl butyrate and about 12 percent cholesteryl formate and about 12 percent cholesteryl decanoate;
- LXXXVIII About 40 percent cholesteryl chloride and about 40 percent cholesteryl butyrate and about 10 percent cholesteryl formate and about 10 percent cholesteryl decanoate;
- LXXXIX About 42 percent cholesteryl chloride and about 42 percent cholesteryl butyrate and about 8 percent cholesteryl formate and about 8 percent cholesteryl decanoate;
- LXXXX About 44 percent cholesteryl chloride and about 44 percent cholesteryl butyrate and about 6 percent cholesteryl formate and about 6 percent cholesteryl decanoate.

The imaging members are imaged as described in Example I, resulting in clearly optically distinguishable images. The imaged members are erased by the methods described in Example II and Example IV.

Any of the compositions of Examples I and V-LXXXX may be used in imaging layers of different thicknesses and on thinner substrates of different materials, which will typically change the exposure times and resultant exposure energies. See Example XC below.

EXAMPLE XC

An imaging member is provided by the method of Example III wherein the imaging composition comprises about 20 percent ABUTA and about 80 percent cholesteryl oleyl carbonate. An imaging layer about 12 microns thick is prepared on an about 2 mil thick black Tedlar substrate, a polyvinyl-fluoride resin film available from DuPont. The layer of imaging composition is sheared and imaged as in Example I, using

an about 50 microsecond exposure of total energy of about 10 millijoules/cm² of area of imaging layer. An optically distinguishable clear image on a blue tinted background is provided by this system.

Although specific components and proportions have been stated in the above description of the preferred embodiments of the thermally induced texture transition liquid crystalline imaging system described herein, other suitable materials and variations of the various steps in this system as listed herein, may be used with satisfactory results and of various degrees of quality. In addition, other materials and steps may be added to those used herein and variations may be made in the process to synergize, enhance or otherwise modify the properties of and uses for the invention. For example, various other mixtures of liquid crystals which will undergo the imagewise texture transition may be discovered and used in the system of the present invention and such mixtures may require somewhat different thicknesses, temperature ranges, and other imaging conditions for preferred results in accordance with the present invention. Likewise, other means of addressing the imaging members may be used with satisfactory results in the present invention.

It will be understood that various changes in the details, materials, steps, and arrangements of elements of which have been herein described and illustrated in order to explain the nature of the invention, will occur to and may be made by those skilled in the art, upon a reading of this disclosure, and such changes are intended to be included within the principle and scope of this invention.

What is claimed is:

1. An imaging method comprising:

providing a layer of imaging composition comprising a material having a cholesteric liquid crystalline mesophase and providing said layer in the cholesteric liquid crystalline mesophase temperature range of said material and in the Grandjean texture state;

applying energy capable of producing a thermal effect in the composition layer, whereby imagewise portions of said composition layer are affected to raise the temperature of the imagewise portions of said composition to a temperature at least about the cholesteric liquid crystalline mesophase-liquid isotropic transition temperature; and cooling the imagewise portions of said composition to a temperature in the cholesteric liquid crystalline mesophase temperature range of said material, whereby said imagewise portions of said composition layer assume the focal-conic texture state, thereby imaging the composition layer.

2. The method of claim 1 wherein said layer of imaging composition is provided on a supporting substrate.

3. The method of claim 2 wherein the supporting substrate is substantially transparent.

4. The method of claim 3 wherein the imaged composition is observed between polarizers with transmitted light, and the transparent substrate is optically isotropic.

5. The method of claim 2 wherein the supporting substrate is opaque.

6. The method of claim 1 wherein said layer of imaging composition is overcoated with a transparent overcoating.

7. The method of claim 6 wherein said transparent overcoating is of thickness not greater than about 10 mils.

8. The method of claim 1 wherein said layer of imaging composition is of thickness not greater than about 250 microns.

9. The method of claim 8 wherein said layer of imaging composition is of thickness in the range between about 1 and about 50 microns.

10. The method of claim 8 wherein the energy applied to the layer of imaging composition is in the range between about 1 millijoule/cm² and about 100 millijoules/cm² of surface area of said layer.

11. The method of claim 1 wherein the energy is applied in imagewise configuration to the layer of imaging composition.

13

12. The method of claim 11 wherein said layer of imaging composition is of thickness not greater than about 250 microns, and the energy applied is in the range between about 1 millijoule/cm² and about 100 millijoules/cm² of surface area of said layer.

13. The method of claim 11 wherein the energy is applied by exposing the layer of imaging composition to radiant energy through a mask in image configuration.

14. The method of claim 13 wherein the source of said radiant energy is a gas discharge lamp.

15. The method of claim 13 wherein the exposure time is not greater than about 10 seconds.

16. The method of claim 1 wherein said imaging composition comprises a mixture of a material having a cholesteric liquid crystalline mesophase and at least one material selected from the group consisting of: materials having a nematic liquid crystalline mesophase, materials having a smectic liquid

14

crystalline mesophase, and mixtures thereof.

17. The method of claim 1 wherein said imaging composition exhibits cholesteric liquid crystalline characteristics in the temperature range between about 20° C. and about 30° C.

18. An imaging method comprising:

a. providing and imaging a layer of imaging composition by the method of claim 1, and

b. thereafter uniformly applying an external force to said imaging member to erase the image by uniformly providing the layer of imaging composition in the Grandjean texture state.

19. A repetitive imaging method comprising repeating steps (a) and (b) of claim 18 a plurality of times using the same layer of imaging composition.

20. The method of claim 1 wherein the layer of imaging composition has a λ_0 in the visible spectrum.

* * * * *

20

25

30

35

40

45

50

55

60

65

70

75