

[54] **LIQUID CRYSTAL IMAGING SYSTEM  
HAVING AN UNDISTURBED IMAGE ON  
A DISTURBED BACKGROUND AND  
HAVING A RADIATION ABSORPTIVE  
MATERIAL DISPERSED THROUGHOUT  
THE LIQUID CRYSTAL**

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252/408, 350/157, 350/160 LC**

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

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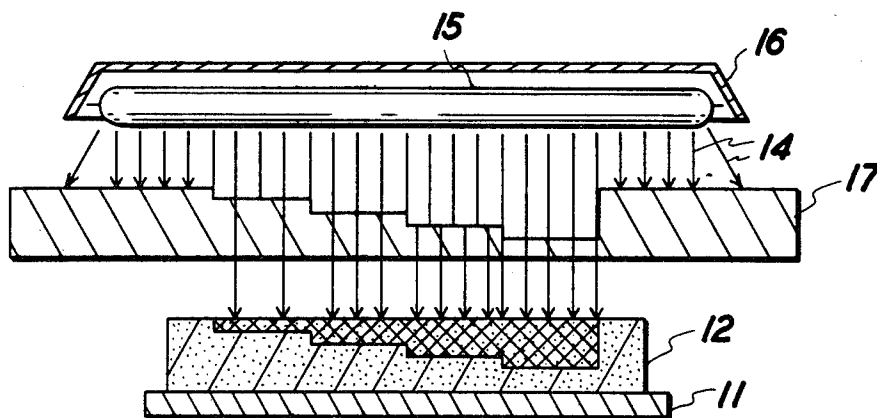
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[57]

**ABSTRACT**

An imaging system wherein an imaging member comprising a composition comprising a material having a cholesteric liquid crystalline phase with radiation absorptive material dispersed throughout the liquid crystalline material, is provided with the liquid crystalline composition in its Grandjean or "disturbed" texture state, and the member is thermally imaged by imagewise heating image portions of said imaging material to a temperature at least about the cholesteric liquid-isotropic transition temperature range of the 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 may be erased, and the imaging members used therein are typically reuseable.

**25 Claims, 7 Drawing Figures**



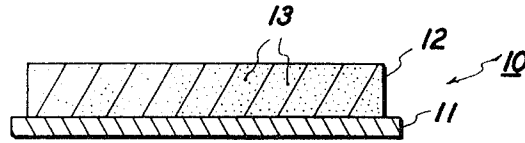


**FIG. 1**

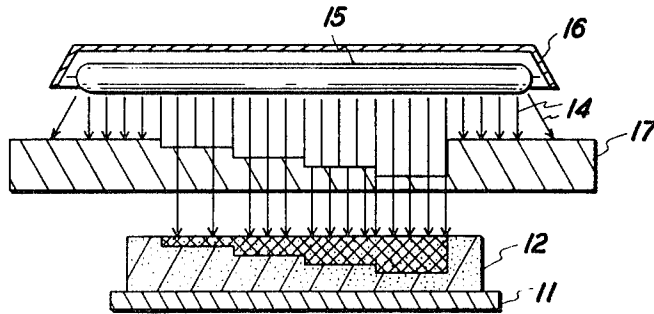


**FIG. 2**

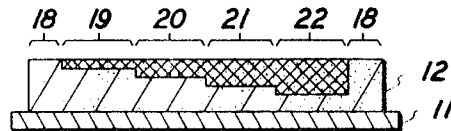


**FIG. 3**

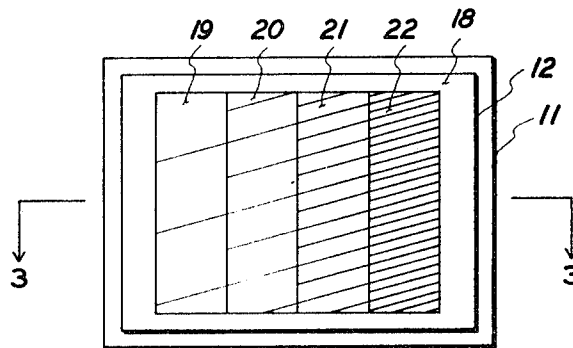


**FIG. 4**

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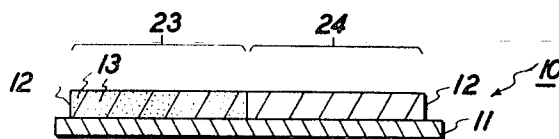


FIG. 5

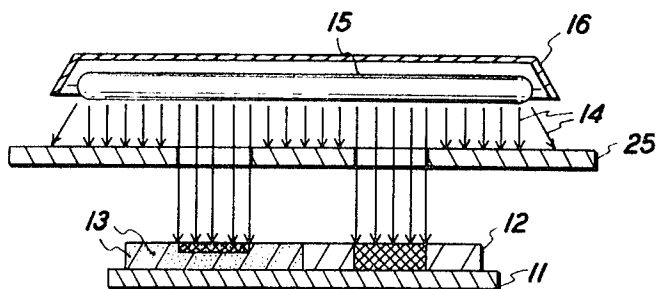


FIG. 6

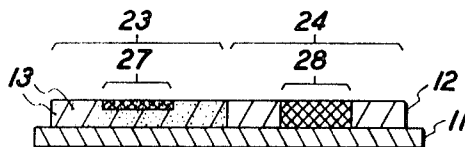


FIG. 7

# LIQUID CRYSTAL IMAGING SYSTEM HAVING AN UNDISTURBED IMAGE ON A DISTURBED BACKGROUND AND HAVING A RADIATION ABSORPTIVE MATERIAL DISPERSED THROUGHOUT THE LIQUID CRYSTAL

## BACKGROUND OF THE INVENTION

This invention relates to imaging systems, and more specifically, to an imaging system wherein the imaging member comprises an imaging material having cholesteric 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 crystalline solids. Liquid crystals exhibit mechanical characteristics, such as viscosities, which are ordinarily associated with liquids. The optical characteristics of liquid crystals are similar to those characteristics ordinarily unique to crystalline 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 cholesteric. 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 U.S. Pat. No. 1,484,584; Fergason 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 Fergason et al. U.S. Pat. No. 3,144,836; Fergason U.S. Pat. No. 3,410,999; Asars U.S. Pat. No. 3,415,991; Woodmansee U.S. Pat. No. 3,411,513, and British Pat. No. 1,153,959.

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.

Cholesteric liquid crystals are known to exhibit various observable textures. For example, cholesteric liquid crystals may adopt a homoeotropic, a focal-conic, or a Grandjean plane texture as modifications of the cholesteric 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 867,593.

Various heat-sensitive, or thermal copy-papers and systems, including systems using radiation absorptive pigments, are known, as exemplified by Kuhmeyer U.S. Pat. No. 2,976,415. The use of additive fillers in liquid crystal compositions to increase the visibility of color patterns exhibited by cholesteric liquid crystal materials because of their selective light scattering characteristics is also known as shown in Woodmansee

U.S. Pat. No. 3,411,513. Fergason U.S. Pat. No. 3,409,404 shows the compatibility of cholesteric liquid crystalline materials with oil additives, and Fergason's article in *Applied Optics*, Vol. 7, No. 9, Sept., 1968, p. 1,730, shows that dyes may be added to cholesteric materials. Dreyer U.S. patent No. 2,544,659, French U.S. Pat. No. 3,440,620, and Goldmacher et al. U.S. pat. No. 3,499,702 disclose nematic liquid crystalline compositions with additives or "guests." However, 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 in new modes. Similarly, further new uses and surprising and advantageous results of uses of such new technology are being discovered. The present invention relates to a new and advantageous system for imaging cholesteric liquid crystalline members.

## SUMMARY OF THE INVENTION

It is, therefore, an 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 a sensitive, continuous tone imaging system.

It is another object of this invention to provide an imaging system of high resolution and contrast density.

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 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 composition comprising a material having a cholesteric liquid crystalline phase with radiation absorptive material dispersed throughout the liquid crystalline material, with the liquid crystalline composition in its Grandjean or "disturbed" texture state, and the member is thermally imaged by imagewise heating image portions of said imaging material to a temperature at least about the cholesteric liquid-isotropic transition temperature range of the 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 may be erased, and the imaging members used therein are typically 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 in the inventive imaging system.

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

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

FIG. 5 illustrates in partially schematic, cross-sectional view, an imaging member having two different areas of differing imaging compositions.

FIG. 6 illustrates in partially schematic, cross-sectional views the imaging member of FIG. 5 being imaged.

FIG. 7 illustrates in partially schematic cross-sectional view, the imaging member imaged in FIG. 6.

#### 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 12 comprising a material which exhibits a cholesteric liquid crystalline mesophase, with particulate radiation absorptive material 13 dispersed throughout the liquid crystalline material.

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 cholesteric liquid crystalline mesophase. Any suitable cholesteric liquid crystal, mixture or composition comprising liquid crystals, or composition having cholesteric 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 vaccenate; 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 $\beta$ -amino- $\Delta$ 5-cholestene and mixtures thereof; peptides such as cholesteryl poly- $\gamma$ -benzyl- $\alpha$  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 doublebonded 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'-nitrophenyl-4-carboxylic acids' ethyl-p-azoxy-cinnamate; ethyl-p-4-ethoxybenzylidene-aminocinnamate; 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 paraamino-phenylacetate, p-ethoxy-benzalamino-a-methylcinnamic acid, 1,4-bis(p-ethoxy benzylidene) cyclohexanone, 4,4'-dihexyl-oxybenzene, 4,4'-diheptyloxybenzene, anisal-p-amino-azo-benzene, anisaldazine, a-benzeneazo- (anisol- $\alpha$ -naphthylamine), n,n'-nonoxybenzotoluidine; anils of the generic group (p-n-alkoxy-benzylidene-p-n-alkylanilines), such as p-methoxy benzylidene p-n-butylaniline, mixtures of the above and many others.

The above lists of material 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 advantageous radiation absorptive material 13 which is typically dispersed throughout the imaging composition layer 12, may comprise any thermally absorptive material, or any material which produces an exothermic effect upon excitation by external radiation. In various embodiments of the inventive system, the radiation absorptive additive material may be particulate and insoluble in the liquid crystalline composition, or soluble or miscible with the composition, or comprise combinations of such materials.

Where the additive comprises involuble particulate material, any such material may be used. For example, a variety of pigments which are substantially insoluble in the liquid crystalline composition may be used. Exemplary particulate additives include carbon black, copper phthalocyanine, benzidine yellow, azure II, cyan blue, methylene blue, Graphitol yellow, aniline blue black; metallic additives such as aluminum, copper, gold, silver, indium, iron, and platinum, mixtures thereof and others.

Where the radiation absorptive additive material is soluble in or miscible with the liquid crystalline composition a variety of dyes may be used. Such soluble or miscible materials generally include most oil soluble materials. Exemplary soluble or miscible additives include anilin blue, available from J.T. Baker, Phillipsburg, N.J.; indigo; methyl red, available from Eastman Kodak, Rochester, N.Y.; Oil Blue N, available from Allied Chemical, Morristown, N.J.; 4-phenylazo-1-naphthylamine, available from J.T. Baker; mixtures thereof as well as others.

Although in various embodiments of the inventive system, any suitable amount of soluble and/or insoluble additive may be used with the liquid crystalline composition, compositions containing not greater than about 20 percent additive are preferred for use and typically give the most satisfactory imaging results. For example, where carbon black is the additive, a preferred range of loading is between about 2.5 percent and about 8 percent, and an optimum range is between about 4 percent and about 6 percent. The optimum loadings give optimum imaging results in terms of contrast and grey scale.

The particulate additives used in the present invention are preferably of average particle size not greater than about 50 microns, and give optimum results when of average particle size not greater than about 5 microns. The smaller particulate additives enhance grey scale quality and resolution in the inventive imaging system.

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 particulate radiation absorptive material is then mixed with the solution containing the liquid crystal material which is then typically poured, sprayed or otherwise applied to the imaging members. After evaporation of the solvent, a thin layer of liquid crystals remain. Alternatively, the individual liquid crystals of the liquid crystalline mixture along with the particulate additive can be combined and applied directly by heating the mixed components above the isotropic transition temperature of the cholesteric liquid crystal components and mixing all the components before application to a suitable substrate.

The liquid crystal imaging layers or films used in the present invention may, surprisingly, be of any thickness.

Where such cholesteric liquid crystal imaging composition layers are used without the advantageous particulate radiation absorption material, the layers or films are preferably of a thickness in the range of about 250 microns or less, and optimum results are typically achieved using such 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 mechanically disturbing it such as by pressure or by shearing stresses, 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  $\Lambda$  where  $\Lambda = 2np$  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  $\Lambda$ . If  $\Lambda$  is in the visible spectrum the composition layer comprising cholesteric liquid crystalline material appears to have the color corresponding to  $\Lambda$ , for normally incident light and observation. If  $\Lambda$  is outside the visible spectrum the composition layer typically appears colorless and non-scattering, or takes on the color of any additives included therein. 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 12 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 heating 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 exposed through a photographic-type grey scale step-tablet mask 17 to thermal radiation 14 which is emitted by a source 15 under shield 16.

In the inventive system the thermal energy which is applied in imagewise configuration to the layer of imaging composition is typically at least in part absorbed by the advantageous radiation absorptive material dispersed throughout the liquid crystalline layer. The absorbed thermal energy increases the temperature of the absorptive material (and at least to some extent increases the temperature of the liquid crystalline material itself) and the temperature increase in the absorptive material due to the preferential absorption of energy by that material is conductively transferred to the liquid crystalline material in very close proximity to any given particle of the radiation absorptive material. In this way, the imagewise portions of the imaging composition layer which have been exposed with the thermal energy, are heated approximately proportionally to the amount of thermal energy to which any given thermally exposed region was exposed. In many of the

imagewise exposed areas the imaging composition comprising the material having the cholesteric liquid crystalline mesophase is locally heated to temperatures above or at least about the liquid crystalline-isotropic transition temperature of the imaging material having the cholesteric liquid crystalline characteristics. After the imagewise application of sufficient thermal energy to raise the temperature of the desired portions of the imaging composition in imagewise exposed areas to a temperature above or at least about the isotropic transition temperature of the liquid crystalline material, 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. Upon cooling into the cholesteric liquid crystalline mesophase temperature range the desired portions of the imagewise exposed areas of the imaging composition which were raised to temperatures at least about the isotropic transition temperature, typically exhibit the focal-conic or "undisturbed" texture state, thereby providing an imaged member having image areas of the 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 or "disturbed" texture state. Where the Grandjean state is substantially transparent, and the advantageous additives of the present invention are used, the Grandjean areas exhibit the color of the additive material.

While in many embodiments hereof the temperature in the areas to be imaged is typically raised to or above the cholesteric liquid crystalline-isotropic transition temperature, it is found that in some embodiments temperatures within a few degrees C. of the transition temperature of the imaging composition, i.e., at least about the 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 are found to cause the desired effect in some embodiments.

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  $\Lambda$  is in the visible spectrum or not. The appearance of the focal-conic texture state is typically milky-white. The focal-conic texture of cholesteric liquid crystalline materials is sometimes referred to as the "undisturbed" texture state.

FIG. 3 illustrates in partially schematic, cross-sectional view, an imaged member wherein the layer of imaging composition 12 exhibits imaged areas 19, 20, 21, and 22 in the focal-conic or "undisturbed" cholesteric liquid crystalline texture state. FIG. 3 illustrates that the Grandjean to focal-conic texture transition imaging system of the present invention is in part a bulk effect in the transformed or imaged areas of the imaging composition. However, surprisingly, in the present invention it is found that the use of the advantageous radiation absorptive material dispersed throughout the liquid crystalline material gives the texture transition imaging system and unexpected increase in sensitivity which facilitates control of the imaging system and increases its capabilities for producing quality, high contrast, high resolution, and even grey scale images. It is particularly notable that the inclusion of the radiation absorptive material allows control of the bulk transformation effect to a specific thickness of the imaging composition in the thermally exposed portions of the composition layer. It is generally expected that the entire thickness of a liquid crystalline imaging composition layer without the absorptive additive will be transformed in such texture transition systems.

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 3c) showing imaged areas 19, 20, 21, and 22 exhibiting different grey-scale tones in the focal-conic texture state surrounded by background areas 18, in the Grandjean texture state. Although the imaged areas 19, 20, 21, and 22 in FIG. 4 cor-

respond to the different gray-scale areas of the photographic step tablet through which the member was exposed, it will be appreciated that any method of imagewise thermally exposing the member may be used to provide any desired imagewise shape or design on such an imaging member. FIG. 4 illustrates that the imaged areas 19-22 are clearly optically distinguishable from the background areas 18, and furthermore, that the inventive imaging system produces continuous tone images having various areas of different contrast densities. Here, for purposes of illustration, the most dense area 22 in the imaged member of FIG. 4 corresponds to the area of the exposure step-tablet which transmits the greatest amount of energy during the exposure step.

Although the images provided by the inventive system are typically of positive optical sense corresponding to exposure through a transparency or mask of negative optical sense, in various embodiments the advantageous additives of the present invention may provide systems capable of producing *p-n*, *p-p*, color and/or color-on-color images. For example, an imaging layer which typically appears green in its unimaged Grandjean state, and may be imaged to provide a clear-on-green image, will provide a black-on-green image when the imaging composition contains a black additive such as dispersed carbon particles. Although the imagewise exposed areas of the imaging composition are the portions which are transformed, various resultant image-background color combinations will give images of different optical senses and different contrast densities. The inventive system typically produces images of contrast densities up to about 2.0, although in some embodiments even higher contrast densities may be achieved. Both the color of the liquid crystalline composition and the included additives contribute to the character of the resultant image. The more transparent or translucent portions of the liquid crystalline composition exhibit the color of the additive. Where the transformed image areas become more translucent or transparent, the density of the color provided by the dispersed additive will typically be proportional to the thickness of the transformed portion of the composition, i.e., the greater the depth of transformation, the greater the image density in the color of the visible additive.

The contrast and image sense of images provided by the inventive system may also be enhanced or changed by observing the image with image enhancing devices such as filters, polarizers, or between crossed polarizers in transmitted light.

The inventive imaging system typically produces images of resolutions up to about 50 line pairs per millimeter, although in some embodiments even higher resolutions may be achieved. Additives of smaller particle size and high color contrast typically facilitate higher resolutions.

It is noted above that it is generally expected that the entire thickness of a liquid crystalline imaging composition layer not having the radiation absorptive additive dispersed throughout the composition will be transformed in texture transition imaging systems such as the one described herein. For purposes of comparison, FIG. 5 illustrates an imaging member 10 wherein the substrate 11 supports a layer of imaging composition comprising a material having cholesteric liquid crystalline characteristics, part of which 23 includes radiation absorptive material 13 dispersed throughout the liquid crystalline composition, and part of which 24, does not contain the radiation absorptive material. FIG. 6 illustrates the member of FIG. 5 being exposed, with approximately equal areas of the loaded area 23 and unloaded area 24 being exposed with approximately the same total energy or exposure through a mask 25. FIG. 7 illustrates in partially schematic cross-sectional view the results of such exposure, wherein the exposed portion 28 of the unloaded imaging composition 24 has been transformed throughout the thickness of the layer of imaging composition 12. Surprisingly, however, in accordance with the present invention, the exposed portion 27 of the loaded portion 23 of the layer of imaging composition, which includes the preferentially radiation absorptive material, is transformed only throughout a portion of the thickness of the imaging composition, as already described above.

It has been found that the presence of the additives of the present invention allows imaging exposures to be made at energy levels which are up to about an order of magnitude less than exposure levels typically used with non-loaded imaging compositions. This extension of the range of suitable imaging exposure energies along with the grey-scale capability of the system (which is also related to the total imaging energy as illustrated by the discussion above) substantially increases the sensitivity of the additive loaded system over similar unloaded systems.

The sensitivity of the inventive system may also be enhanced in another way. When the inventive system is operated in conditions where the imaging composition is substantially uniformly at a temperature which is just a few degrees below the temperature which produces the imaging effect hereof in the desired image areas, the imagewise addition of energy which is added to cause the desired imaging effect is a relatively small amount of energy. In this way, the imaging system may be made sensitive or responsive to imagewise inputs of relatively low amounts of energy. The pre-imaging uniform maintenance of the imaging composition at a temperature near the effective imaging temperature is sometimes referred to as "thermally biasing" the system.

An 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 certain imaging compositions preferred for use under certain conditions. When the present system is used at room temperature, 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. For example, mixtures of between about 30 percent and about 70 percent oleyl cholesteryl carbonate and between about 70 percent and about 30 percent *p*-methoxy benzylidene-*p*'-*n*-butylaniline with about 4-6 percent carbon powder added, or, mixtures of between about 30 percent and about 70 percent cholesteryl erucate and between about 70 percent and about 30 percent *p*-methoxy benzylidene-*p*'-*n*-butylaniline with about 4-6 percent carbon powder added, are preferred room temperature imaging compositions. It is also usually preferable to use imaging compositions whose 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.

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 reuseable 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. 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, substantially transparent, 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 sources 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. Similarly, conductive radiation absorptive material dispersed in the imaging composition layer itself may be used with RF microwave exposure, X-ray exposure, or electron beam address systems to provide the desired heating effect in the inventive system.

The imagewise exposed areas of the imaging composition in inventive system are subjected to energy inputs which are typically in the range between about 1 and about 100 millijoules/cm<sup>2</sup> 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, flash imaging mode of the present invention is particularly advantageous because of its speed, which alters the time in which lateral thermal conductivity can take place and thereby typically enhances resolution in the inventive imaging system. Such short duration exposures are generally less than 10 seconds in duration. Of course, prudent selection of imaging compositions and substrates helps inhibit the lateral thermal conduction and thereby correspondingly enhances resolution in the inventive system.

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, with radiation absorptive material dispersed throughout the liquid crystalline material, 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 composition including particulate radiation absorptive material dispersed throughout a layer of material having cholesteric liquid crystalline characteristics is provided by first preparing a mixture of about 50 percent p-methoxy benzylidene-p'-n-butyl-aniline, a room temperature nematic liquid crystal, and about 50 percent oleyl cholesteryl carbonate, a room temperature cholesteric liquid crystal. This mixture has cholesteric liquid crystalline characteristics and a cholesteric-liquid isotropic transition temperature of about 27.7° C. To this mixture about 5 percent by weight of Carbolac-2, a carbon black powder manufactured by Cabot, is added, and the mixture thoroughly agitated to disperse the radiation absorptive carbon particles throughout the

cholesteric liquid crystalline composition. This imaging composition is deposited on a substrate, here a glass slide, and overcoated with a thin transparent cover plate or film, here a glass cover slide.

Before exposure the layer of imaging composition is provided in the Grandjean texture state by displacing the cover plate or film with respect to the substrate thereby shearing the liquid crystalline imaging composition. A photographic step tablet having density difference steps of about 0.3 is placed on the overcoating surface of the imaging member, and a short duration flash from a Xenon gas discharge flash lamp exposes the imaging member to energy greater than about 11.0 millijoules/cm<sup>2</sup> in any area which it is desirable to image. A grey-scale image corresponding to the step tablet is immediately visible.

Image density is about 1.5, and image contrast density about 1.3 at 5,460 Angstroms. Resolution is about 28 lines per millimeter where exposures are about 27.0 millijoules/cm<sup>2</sup>. Gray scales are achieved in four out of 11 of the steps of the step tablet with density differences of about 0.3.

#### EXAMPLE II

The imaged member prepared by the methods of Example I is instantaneously erased by slightly laterally displacing the overcoating cover slide or film thereby shearing the cholesteric liquid crystalline composition, which erases the image from the composition and restores the composition to its Grandjean texture state.

#### EXAMPLES III - IV

Imaging compositions having cholesteric liquid crystalline characteristics are prepared as in Example I using the following compositions:

III About 70 percent oleyl cholesteryl carbonate and about 30 percent p-methoxy benzylidene-p'-n-butylaniline (hereafter ABUTA) to which about 4 percent Carbolac-2 is added;

IV About 60 percent oleyl cholesteryl carbonate and about 40 percent ABUTA, to which about 4 percent Carbolac-2 is added;

V About 40 percent oleyl cholesteryl carbonate and about 60 percent ABUTA, to which about 4 percent Carbolac-2 is added;

VI About 30 percent oleyl cholesteryl carbonate and about 70 percent ABUTA, to which about 4 percent Carbolac-2 is added.

The layers of imaging composition are provided in the Grandjean texture state, and a black and white photographic negative is placed on the overcoating surface. The members are exposed as in Example I providing continuous tone images corresponding to the photographic negative.

#### EXAMPLES VII - XII

Imaging compositions having cholesteric liquid crystalline characteristics are prepared as in Example I using the following compositions:

VII About 70 percent cholesteryl erucate and about 30 percent p-methoxy-p'-n-butylaniline (hereafter ABUTA), to which about 3 percent Carbolac-2 is added;

VIII About 60 percent cholesteryl erucate and about 40 percent ABUTA, to which about 3 percent Carbolac-2 is added;

IX About 50 percent cholesteryl erucate and about 50 percent ABUTA, to which about 3 percent Carbolac-2 is added;

X About 40 percent cholesteryl erucate and about 60 percent ABUTA, to which about 3 percent Carbolac-2 is added;

XI About 30 percent cholesteryl erucate and about 70 percent ABUTA, to which about 3 percent Carbolac-2 is added;

XII About 14 percent cholesteryl erucate and about 86 percent ABUTA, to which about 3 percent Carbolac-2 is added.

Layers of imaging composition are prepared as in Example I and provided in the Grandjean texture state. A photographic

negative is placed on the overcoating surface, and the members are exposed as in Example I providing continuous tone images corresponding to the photographic negative. Representative resultant images are:

- VIII black image areas on blue background;
- IX black image areas on green background;
- X black image areas on red background;
- XII black image areas on clear (or greyish) background.

#### EXAMPLE XIII

Imaging compositions having cholesteric liquid crystalline characteristics are prepared as in Example I using the following compositions which include Oil Blue, a dye which is soluble in the liquid crystal components of the composition which is available from Allied Chemical, Morristown, N.J., as the radiation absorptive additive:

XIII About 25 percent cholesteryl chloride and about 75 percent cholesteryl nonanoate, to which about 5 percent Oil Blue is added;

XIV About 30 percent cholesteryl chloride and about 70 percent cholesteryl nonanoate, to which about 5 percent Oil Blue is added;

XV About 35 percent cholesteryl chloride and about 65 percent cholesteryl nonanoate, to which about 5 percent Oil Blue is added.

Layers of imaging composition are prepared as in Example I and provided in the Grandjean texture state.

The imaging members having the above compositions are thermally biased to a temperature of about 45° C. on a heating plate. The members are then imaged as in Example I thereby providing continuous tone or grey-scale images corresponding to the step-tablet mask, and the images exhibit the following colors:

- XII blue image areas on green background;
- XIV blue image areas on yellow-orange background;
- XV blue image areas on red background.

#### EXAMPLE XVI

The imaged members prepared by the methods of Examples XIII-XV are instantaneously erased by applying pressure throughout the area of the overcoating slide, thereby also uniformly providing the compositions in the Grandjean texture state.

The above examples are representative of the host of imaging compositions which may be used in conjunction with the advantageous radiation absorptive additives of the present invention. Other suitable imaging compositions having cholesteric liquid crystalline characteristics, to which the advantageous additives may be added are disclosed in copending application Ser. No. 104,348, filed Jan. 6, 1971, (D/2578, filed on the same day as the instant application) the entire disclosure of which is hereby incorporated by reference in the present specification.

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 radiation absorptive additives and other means of addressing the imaging members may be used with satisfactory results of 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, with radiation absorptive material dispersed throughout the composition, 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 the composition layer are affected to raise the temperature of at least a surface layer of the imaging composition in the imagewise portions to a temperature at least about the cholesteric liquid crystalline-isotropic transition temperature of said composition; and cooling at least the imagewise portions of said composition to a temperature in the cholesteric liquid crystalline mesophase temperature range of said material, whereby at least said surface layer of the imaging composition in the imagewise portions of the composition layer assume the focal-conic texture state.
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 1 wherein the radiation absorptive material is particulate material of average particle size not greater than about 5 microns.
6. The method of claim 5 wherein the radiation absorptive material is particulate material of average particle size not greater than about 1 micron.
7. The method of claim 1 wherein the radiation absorptive material is particulate material which is substantially insoluble in the cholesteric liquid crystalline material.
8. The method of claim 1 wherein the radiation absorptive material is soluble in or miscible with the cholesteric liquid crystalline material.
9. The method of claim 1 wherein the radiation absorptive material comprises not greater than about 20 percent of the imaging composition.
10. The method of claim 1 wherein said layer of imaging composition is of thickness in the range between about 1 and about 50 microns.
11. The method of claim 1 wherein said layer of imaging composition is overcoated with a substantially transparent overcoating.
12. The method of claim 11 wherein said substantially transparent overcoating is of thickness not greater than about 10 mils.
13. The method of claim 1 wherein the energy applied to the layer of imaging composition is in the range between about 1 millijoule/cm<sup>2</sup> and about 100 millijoules/cm<sup>2</sup> of surface area of said layer.
14. The method of claim 1 wherein the energy is applied in imagewise configuration to the layer of imaging composition.
15. The method of claim 14 wherein the energy is applied by exposing the layer of imaging composition to radiant energy through a mask in image configuration.
16. The method of claim 15 wherein the source of said radiant energy is a gas discharge lamp.
17. The method of claim 15 wherein the exposure time is not greater than about 10 seconds and wherein the source of said radiant energy is a Xenon gas discharge lamp.

18. 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 crystalline mesophase, and mixtures thereof. 5

19. The method of claim 1 wherein the imaging composition comprises a mixture of oleyl cholesteryl carbonate and p-methoxy-benzylidene-p'-n-butylaniline.

20. The method of claim 1 wherein the imaging composition comprises a mixture of cholesteryl erucate and p-methoxy-benzylidene-p'-n-butylaniline. 10

21. 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. 15

22. The method of claim 1 wherein before applying the energy to produce the imagewise effect, the layer of imaging

composition is thermally biased to a temperature not greater than about 5° C. below the isotropic transition temperature of the composition.

23. 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.

24. A repetitive imaging method comprising repeating steps a and b of claim 23 a plurality of times using the same layer of imaging composition.

25. The method of claim 1 wherein the layer of imaging composition has a  $\Lambda$  in the visible spectrum.

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