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NASA GENERAL WORKING PAPER

CHOLESTERIC LIQUID CRYSTALS AND THEIR APPLICATION TO SPACE TECHNOLOGY

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MANNED SPACECRAFT CENTER

HOUSTON, TEXAS

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ABSTRACT

The unique properties of cholesteric liquid crystals and a number of applications involving their use for space related developments are described. Emphasis is given to one of the more interesting applications, that of a high temperature measurement device for use on the Apollo EVVA (Extravehicular Visor Assembly). Discussions are presented which give the wide usage of the various types of this class of compound for measuring and providing visual, chromatic detections of temperature of materials requiring as much as 1° C resolution and a range of coverage in excess of 100° C. Examples considered and given in this paper include application for temperature measurements of electronic parts, skin, and other parts of biomedical interest; use as a detector for on-off indication, surface and subsurface flaws, and micro energy.

CHOLESTERIC LIQUID CRYSTALS AND THEIR APPLICATION TO SPACE TECHNOLOGY

By Marvin H. Perry

INTRODUCTION

There are presently many different types of sensors used to measure temperature. The most widely used sensors are the thermocouples and thermistors. Infrared radiometers and scanners have recently been introduced for specific uses in remote detection of temperatures on test subjects or materials. Other approaches to measure surface temperature have been the use of temperature-indicating paints and phosphors. These undergo various physical changes at a given temperature which result in a change in color or variations in the intensity of emitted light.

A phenomenon which has recently been introduced to measure temperature changes is a class of organic compounds known as liquid crystals. These compounds may have many advantages in determining the temperature of materials used for spacecraft applications and possibly some biomedical uses. They can be used to visualize directly the surface under study. The thermal sensitivity of liquid crystals is such that it should be possible to use these materials in many thermal tests formerly requiring the use of radiometers. These cholesteric compounds are relatively inexpensive and their wide usage would have an economical advantage opposed to other temperature-sensing devices. Although these substances are deteriorated by ultraviolet light, materials can be used to minimize this effect where it is required. Techniques are also being introduced to encapsulate these substances such that a bondable temperature sensor may be directly applied to many assorted materials. The properties and various applications of these cholesteric liquid crystals will be shown.

LIQUID CRYSTALS

Liquid crystals are cholesteric compounds, and are also called mesomorphs, mesophases, or mesoforms. This group of compounds, when properly prepared, exhibit changes in color with changes in temperature.

These substances are in a state of matter intermediate between solid and isotropic liquids. The color scattered by the liquid crystals is unique for a specific temperature, thus allowing the quantitative measurement of temperature. By applying these crystals to an object, its temperature change can be observed. The color change is reversible and will follow minute changes in temperature. As these materials are heated they will change color from clear to red, orange, yellow, green, blue and finally back to clear again. The temperature at which a specific color occurs and the temperature range from red to blue may be varied to cover a large number of applications by the proper choice of cholesteric compounds. To date, liquid crystals have been tested at temperatures up to 163° C. Liquid crystals scatter the incident light selectively rather than absorbing it, therefore a dark or black background is advantageous for an enhanced response. A water-soluble black paint is generally used. The liquid crystals may be dissolved in an organic solvent and sprayed or brushed onto a surface, or since many of these mixtures are liquid at room temperatures, the material may be brushed on directly without a solvent.

Matter is thermodynamically classified into one of three phases -- solid, liquid or gaseous. While this classification ordinarily identifies the mechanical characteristics of a material, it does not necessarily identify its molecular arrangement. For this amorphous state, molecules form in random array and remain in random motion. In the crystalline state, molecules are firmly fixed in a three-dimensional crystal lattice.

In an intervening mesomorphic state (liquid crystal), large groups of molecules are able to move and turn about, yet retain some structural arrangement. Such mesomorphic substances simultaneously have properties of liquids and solids. The properties and combinations, however, are so diverse that subclassification is required. The cholesteric phase is such a subgroup.

Whereas ideal liquids would be optically isotropic, i.e. their optical properties are the same measured in all directions, liquid crystals exhibit optical characteristics similar to birefringent crystals, which are optically anisotropic. Their optical properties depend on the orientation of the crystal structure. The color response is the result of many randomly oriented regions, i.e., ordered areas that are spontaneously anisotropic.

The color change of cholesteric materials is directly related to a change of shape of the delicately balanced component molecules. Upon heating, the helical twist of the overall molecular configuration alters. (See figure 1.) This temperature dependence of the liquid crystals optical properties is inherent and reversible.

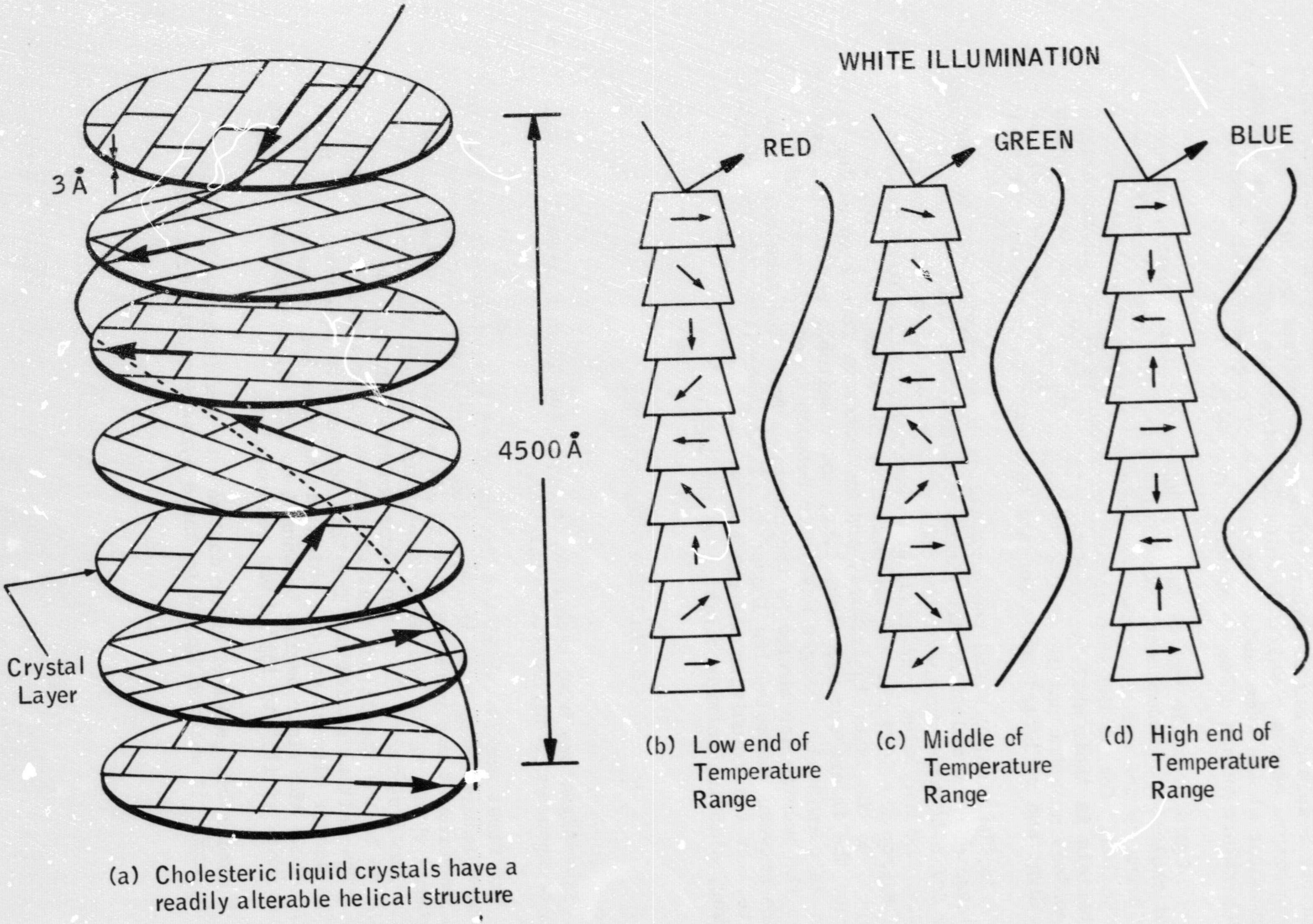

Figure 1.- Effect of heat on liquid crystals.

The crystals selectively reflect only one wavelength at each angle and the resulting mix of colors is seen as iridescence. The change in temperature causes a shift in molecular structure and, thus, a different color at the same angle. An example of a generalized curve of temperature versus color is shown in figure 2.

Liquid crystals may be further subdivided into nematic, smectic, and cholesteric mesophases, according to the different birefringent patterns or texture which these compounds exhibit while being heated or cooled. One of the more attractive features of the cholesteric materials is their ability to reflect light at different wavelengths dependent upon the nature of the cholesteric substance, the angle of incident and reflected radiation and the temperature of the material.

In the nematic state the crystalline layer arrangement no longer exists, and the molecules are simply arranged parallel, but without any definite arrangement of the ends of the molecules. In the smectic state, the molecules (rod-like) are arranged parallel to one another, in layers; the long axes of the molecules lie normal or tilted with respect to the layer interfaces, and the cohesive forces operating across the interfaces are weak, i.e., under suitable conditions, layer flow is permitted. Changes may occur between these two patterns in that the smectic can change to the nematic form. The terminal attractions between the molecules loosen to allow layer flow into the smectic state. At the transition the primary lateral attractiveness must loosen, allowing interpenetration of the layers.

APPLICATIONS UNDER STUDY

Investigations have been made to apply the liquid crystal phenomenon to spacecraft and related equipment.

The first problem which was investigated was to detect and monitor the temperature changes on the EVVA (extravehicular visor assembly). This measurement was required to warn the astronaut of excessive temperatures which may be caused by direct and reflected solar radiation on the lunar surface. The conditions under which this may occur were likely to be the conditions most advantageous for scientific exploration. The initial guidelines for this temperature measurement were a passive sensor element and one which has an area less than one square inch. Since the visor begins to anneal at 125° C, a temperature sensor with a range of 113° to 135° C was recommended.

A sensor was produced under contract to Westinghouse Electric Corporation. It was configured to three symmetric dots arranged in a

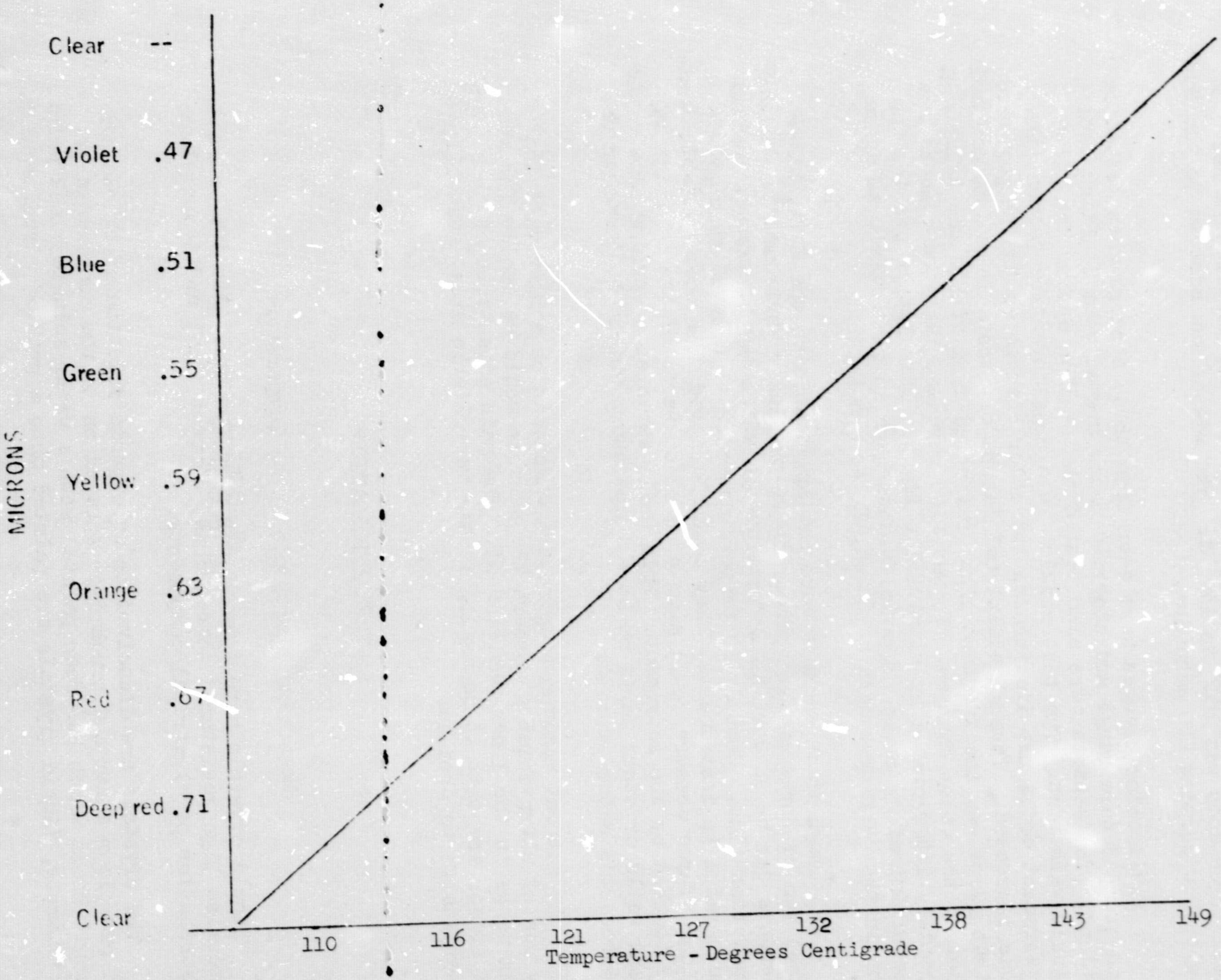

Figure 2.- Color - temperature curve.

pyramid shape. Each dot would change color at a discrete temperature, because of the cholesteric compounds used. The temperature range of all three dots was 100° to 135° C. The sensor was adhered to the EVVA with Dow Corning 280 adhesive.

Vivid color changes were seen from these sensors when tested over the temperature range and observed under normal room lighting conditions. The sensors were also tested on the EVVA during the fifth lunar walk test. The test results were unsatisfactory because the astronaut could not distinguish the color changes as the temperature was increased. Through additional laboratory tests it was determined that there was insufficient light reflected from within the helmet to detect the color changes. It was also revealed that the sensors are readily deteriorated by ultraviolet light. This latter problem can be minimized by using ultraviolet absorbers in cholesteric solution or in the carriers, such as Lexan, Mylar and Kapton.

Although these sensors were not applicable to the EVVA, other uses can be foreseen for spacecraft in the lunar environment. These sensors can be used on ALSEP instruments which may be exposed to high radiation flux. Should the temperature rise to a level which would be harmful to instruments, they could be moved to a more suitable location. These sensors could also be used on parts of the LM which may be touched by the astronaut. This would serve as a warning should the hand rails or other parts be at a temperature which may endanger the astronaut's outer garments.

The current maximum temperature which can be achieved is 163° C. By use of ultraviolet absorbers the sensors would be usable for about six weeks in the lunar environment. The main advantages of this type of sensor are that it is small, it has very little mass, and will be inexpensive to produce.

OTHER APPLICATIONS

Measuring Electronic Parts Temperature

Liquid crystals have been widely used for more than two years to determine high resistance connections, current flow, and temperature distribution of electrical components.

The crystals are dissolved in an organic solution of chloroform and petroleum ether and brushed or sprayed on to the components or circuit board which has been painted with a water soluble black paint. For example, liquid crystals are painted onto a printed circuit which has an apparent high resistance solder joint, or welded connection. By passing current through the circuit and observing the color changes on the surface of the board the high resistance connection can be easily detected. The hot connection would be at a different color than the rest of the circuit. (See figure 3.) Similar techniques can be applied to specific components such as resistors. Although no particular significance can be attached to the temperature profiles (figure 4), it has been suggested that resistors having nonuniform temperature distribution may have shorter life expectancy because of impaired heat dissipation. This type of testing would be advantageous to quality assurance organizations.

Measuring Skin Temperature

A technique has been developed whereby temperature gradients can be measured on the surface of the skin. The use of liquid crystal for this application is somewhat different because the temperature of interest is very low. The total temperature is only 3° or 4°, primarily between 32° and 36° C.

In order to fully utilize this technique, parameters which have been neglected in the other discussions need to be considered. This is required to accurately resolve some temperature resolution. The parameter which is critical is an exact measurement of the wavelength and the incident angle. The technique requires an interference filter which expands the incident light and a spectrometer to accurately measure the wavelengths to determine the temperature variations.

The skin is blackened with a water solution of carbon black to enhance the color array. As in other cases, the cooler temperatures are red. As the temperature increases, the colors progress to yellow, green, and then to blue, from wavelengths of 650 millimicrons to 450 millimicrons. These isothermal patterns can be studied by photographing the area through a narrow band interference filter using a light source which contains the wavelengths transmitted by the filter. Consider a Hg green filter (546 millimicrons). Since the light it transmits lies in the center of the visible spectrum, it will allow for shifts in either direction. (See figure 5.)

As previously mentioned, to accurately measure the temperature attention must be given to the geometric relationships of the setup. The color scattered to the photographic lens depends not only on the temperature but on the angle of the light source and the angle of the axis of the lens with respect to the surface of the skin. Because the temperature-wave-length curves for the liquid crystal mixtures are derived from normal incident lighting, a correction in wavelength must be made before the temperature from these curves can be recorded with

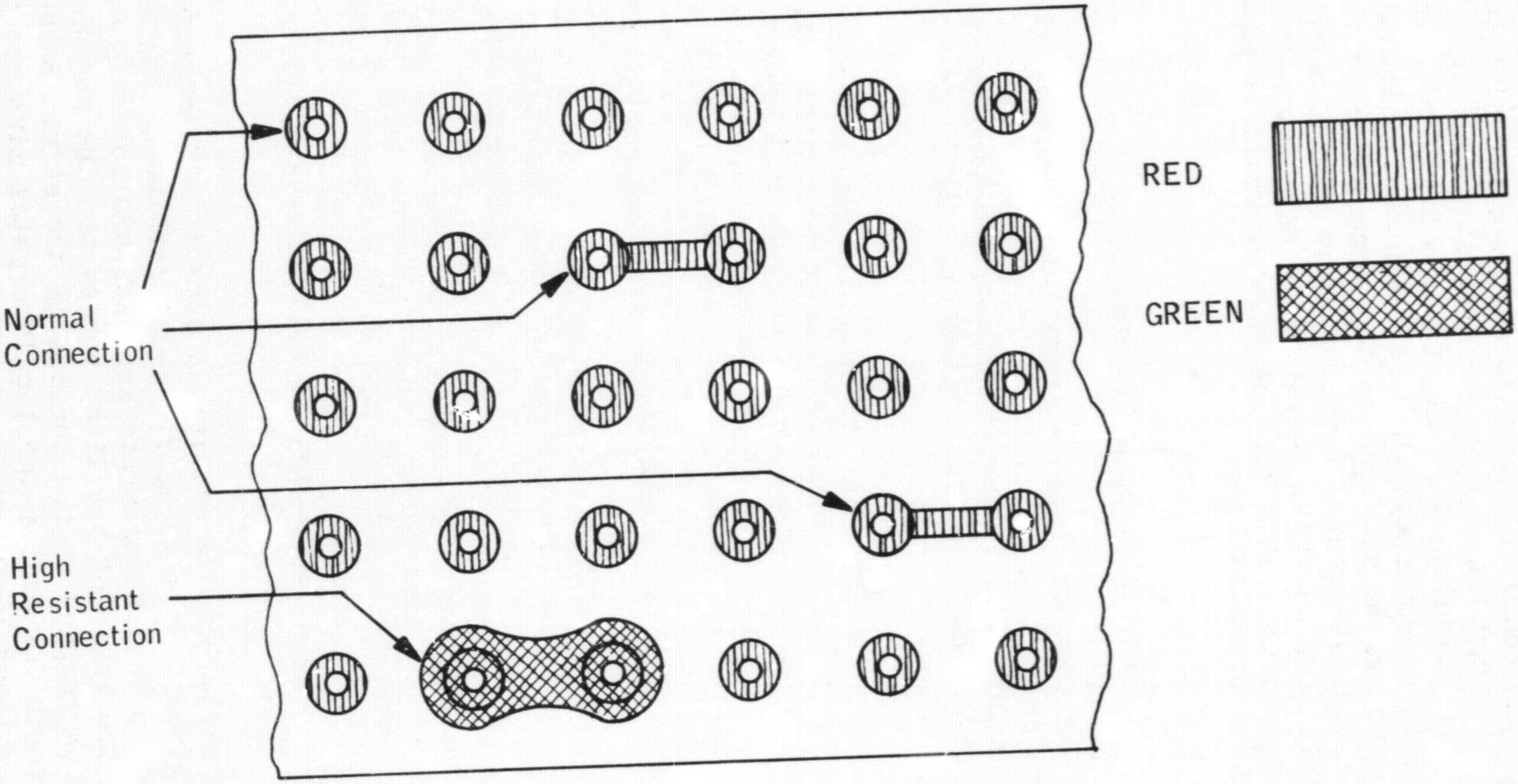

Figure 3.- Detection of high resistance connection on circuit boards.

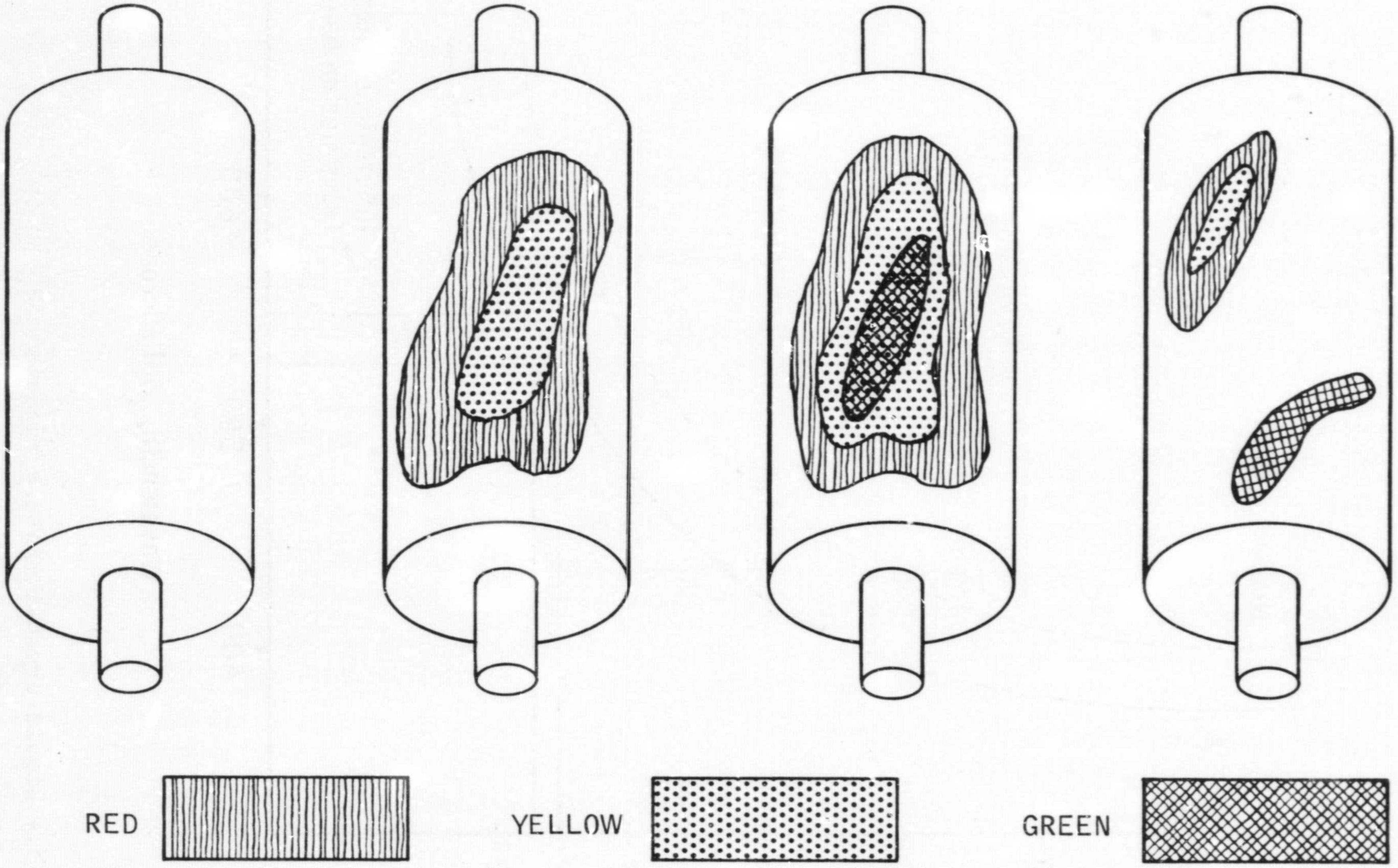

Figure 4.- Typical temperature distribution patterns found in resistors.

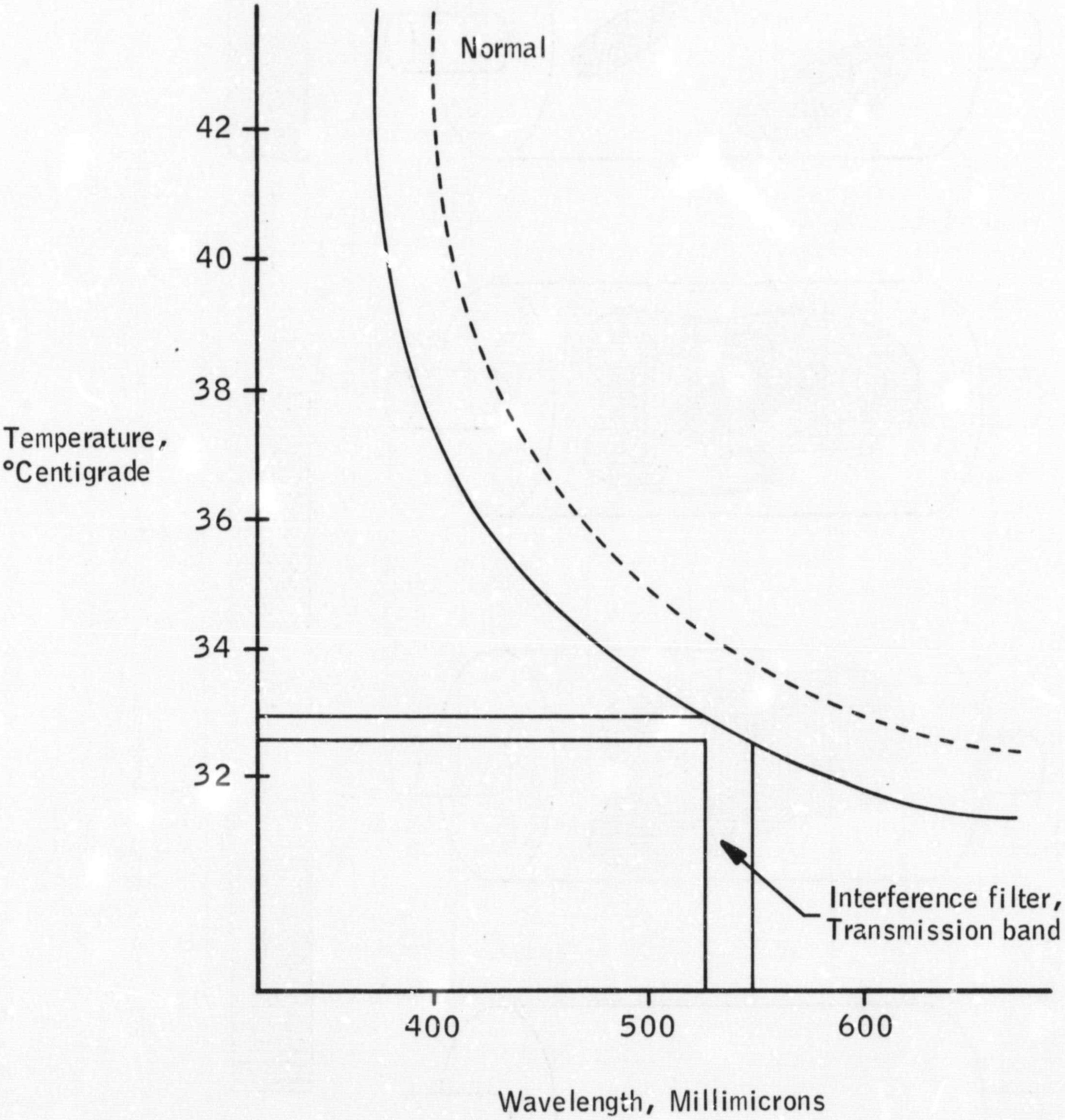

Figure 5.- Liquid crystal mixture adjusted 32° to 35° C.

the best accuracy. The experimental fields which reflect wavelengths transmitted by the filter are recorded on the film. A comparison of negative densities, (white areas on the positive print) with the temperature curve of the mixture of the liquid crystals used will indicate the temperature which existed within these areas when the photograph was made. The precision of the measurement is directly related to the width of the transmission band of the interference filter. By using various filters which can be preselected, all points existing at any temperature can similarly be recorded.

This technique has been successfully used to localize and diagnose abnormal tissue and growth in humans and animals. It has also been used in studying peripheral blood vessels. Similar applications can be used where accurate temperature measurements are required over a broad area in a narrow temperature band.

Detection of Surface and Subsurface Flaws

A material which has a cracked surface or a flaw may inhibit the flow of heat sufficient to produce an appreciable distortion in a normal temperature pattern produced from a point source of heat. Figure 6 illustrates a cracked panel which has been coated with a layer of liquid crystals. When the heat flow reached the crack, a definite buildup in temperature on the side near the heat source and a low temperature region on the other side of the crack could be observed. Similar results were obtained with a steel weld which contained a number of very tight cracks which were difficult to detect visually but were readily seen by use of the liquid crystals. It would seem feasible that gross subsurface flaws can also be detected by this technique. A void located close to the surface of a weld, for example, will produce a transient hot spot as the surface is heated. The reduced mass of material over the void would result in local excess temperature until heat flow produces a uniform surface temperature. Similar techniques can also be used to detect adhesive bands and honeycomb panels.

When one side of a panel is heated, the heat distribution being equal, the detection of a poor bond or no bond can be made again by the color changes in the liquid crystals on the opposite side of the panel. In this case, the cold spots exhibiting a red or green color would indicate a deficient bond.

On-off Indicators

Liquid crystals have been found useful as on-off indicators. This application can be readily seen for panel readouts, etc. The most

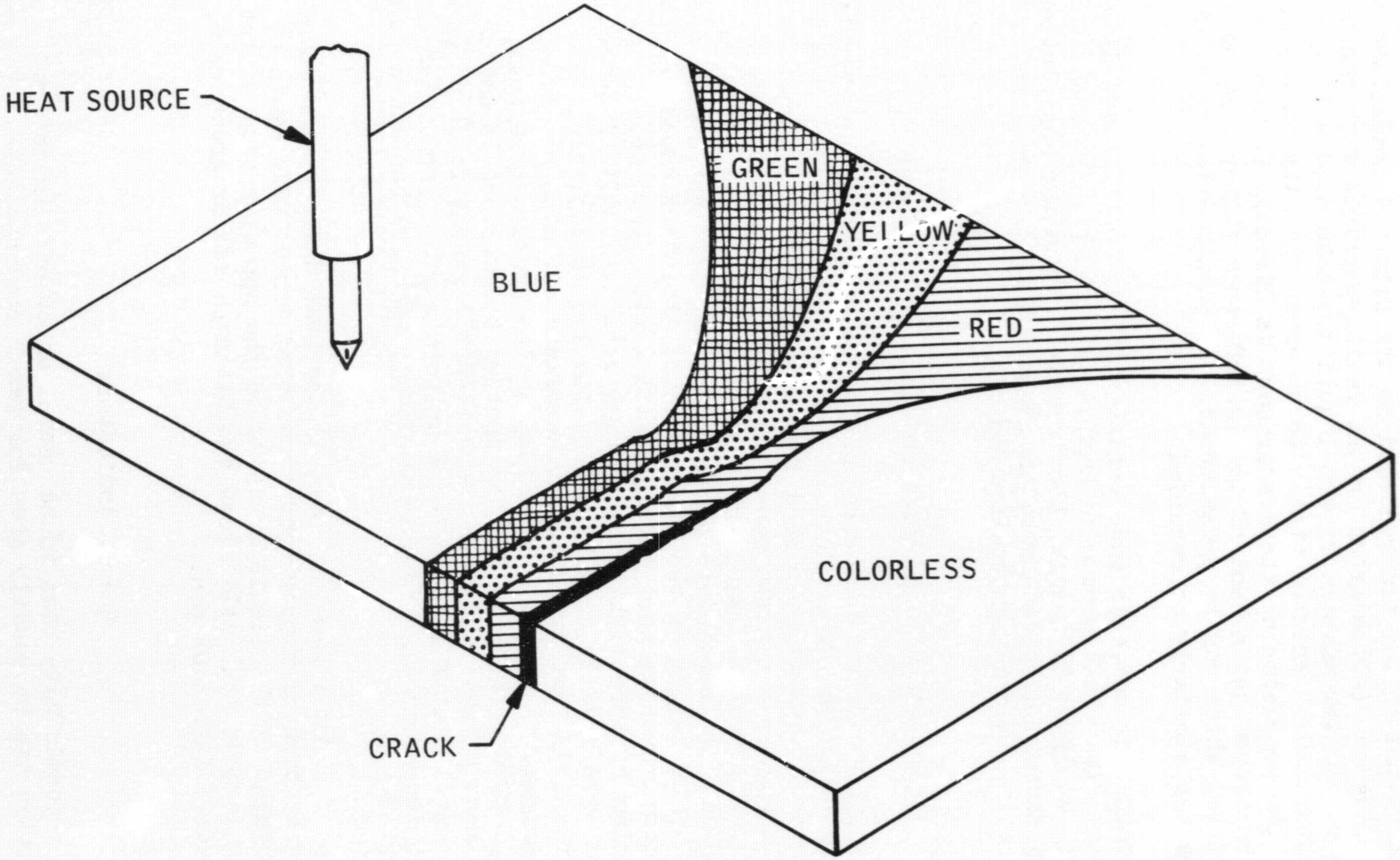

Figure 6.- Crack detection using liquid crystals.

significant application would be in the detection of switching circuits, such as NAND gates. Another application is the detection of an on-off condition of silicone controlled rectifiers in various microcircuits. These applications are numerous and are readily adaptable to microcircuit and digital circuit analysis.

Microwave Energy Detection

The Bendix Corporation has developed a technique using liquid crystal as the sensing element in a broadband microwave detector. This detector will instantly display the field intensity which can readily be photographed. It can also be used to plot near-field antenna patterns in complex waveguides and resonators and to measure impedance and power by detecting standing waves and power density patterns in open transmission lines.

The test setup consists of a support structure made from a very thin 2 mil Mylar membrane. A thin metalized film was deposited on the membrane. A good heat conductor such as nichrome should be used. Approximately 400 ohms per square foot is an acceptable resistance. This film is then coated with a layer of liquid crystals.

A concentrated microwave beam passing through the membrane sets up currents in the metalized film. Energy transferred to the film heats up various segments in proportion to the amount of energy that is absorbed. Distinct color lines surround the area through which energy was transmitted. These lines form a two-dimensional plot of the microwave field intensity.

The membrane was placed about 1 inch in front of a radiation waveguide. When the energy level is raised to about 20 milliwatts, distinct oval concentric bands of color will appear on the membrane. The temperature range represented by the transition from blue to red is equivalent to a power spread of 7 decibels. The shape of the beam is well defined. The shape can be expanded or contracted by adjusting the amount of power from the waveguide. The energy density of the beam can be calibrated by comparing the difference in radiated power to the change in position of a particular color.

The technique using the liquid crystal membrane might possibly also serve as a basic element in a microwave fluoroscope. This apparatus could then be used to find internal flaws or changes in density or thickness of materials that are translucent to microwave radiation.

The active component required would be a microwave signal source. This source should be at X band or above and be capable of delivering several watts of average power to the power divider. Two wavelengths of waveguides would feed two collimating antennas opposite each other and a foot or more apart. There would be lens-compensated horns with several hundred square inches of radiating surface. These radiate essentially plane waves in the near field.

The plane wave, traveling in opposite directions, creates a standing wave between the antennas. Ideally, standing waves have troughs and peaks in planes perpendicular to the direction of propagation. If a liquid crystal membrane is placed completely in the plane of a standing wave trough, minimum energy would be absorbed and the membrane color would correspond to a minimum temperature (red).

As the membrane is moved from a trough toward a peak, the color changes as a result of a higher temperature. The membrane would have a uniform color as long as it was kept in a plane perpendicular to the radiation. Similarly, if a sheet of uniform dielectric material was inserted between one antenna and the membrane, the membrane color would change because of the added phase shift, but remain uniform. However, if the dielectric material were not uniform, the membrane would display contours of color caused by areas on the material having significant deviations in phase or loss. Absolute differences in loss or phase can be determined with a calibrated waveguide phase shifter or attenuator inserted ahead of one antenna.

For some measurements, it may be desirable to place the membrane at an angle to the direction of propagation. This would cause a series of identical color bars to appear across the sheet. The number of bars depends on the angle of the sheet and the microwave frequency. Now any nonuniformities cause irregularities to appear in the color bars. This presentation gives some indication of depth as well as cross section. Also, a number of membranes placed at right angles to each other could be used to construct three-dimensional images in space.

Variations from a plane surface or just the reflector can be detected, as well as variations in such materials coated on metals, cork, and plastic paint.

DISCUSSION

The application techniques which have been discussed are largely within state-of-the-art. A great deal of work has been accomplished by industries and universities to develop the capability of these cholesteric compounds. The majority of the effort has been accomplished with those compounds which are active between 20° and 40° C. The compounds which are available in this range may be procured with a minimum of 3° C and to a maximum of 10° C resolution. The work in the high temperature crystals has been accomplished within the last 15 months. The resolution of high temperature compounds is considerably higher (100° to 170° C). This resolution can be narrowed; however, the first indications reveal that a 20 percent hysteresis is introduced by mixing the various cholesteric compounds.

Although the optical properties of these cholesteric compounds have been known for more than 75 years, the industrial applications have progressed within the last three to four years. These techniques which have been described are now widely used. The work recently accomplished at the Manned Spacecraft Center and Westinghouse Research Center was an added link to the knowledge chain in this field. The primary contributions were in the evaluation of the compounds in a vacuum environment and the use of the high temperature crystals.

Research is being conducted in medical laboratories on cholesterol compounds found in animals. Although the liquid crystal substances are rarely found in living animals, there has been evidence that further detection may be accomplished soon.

In the recent investigation accomplished by the Space Electronic Systems Division on the application of liquid crystals to the EVVA, it was evident that the use or knowledge of these compounds and techniques are not readily known. Hopefully this report will bring the applicable uses of these compounds to the attention of the various organizations of the MSC, and invite their further exploitation.

CONCLUSIONS

Liquid crystal compounds can be useful in monitoring temperatures in different ranges from 20° to 163° C. Variations of these mixtures make it possible to adjust the temperature at which the color changes occur. The visual color changes are vivid in normal room lighting. These compounds are readily available and inexpensive and may be used for applications which were previously accomplished by costly and sophisticated instrumentation. These mixtures can be encapsulated and adhered to most all types of material. This type of sensor has very little mass, is economical and passive. These factors suggest that further and more widespread application of the cholesteric liquid crystals could prove highly beneficial.

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