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**Methods for Creating a Multi-Axis Polarizer for Visible Light
Attenuation by Linear Translation**

Peter L. Donatelli

Thesis submitted to the
College of Engineering and Mineral Resources
At West Virginia University
In partial fulfillment of the requirements
For the degree of

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In
Aerospace Engineering

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Abstract

Methods for Creating a Multi-Axis Polarizer for Visible Light Attenuation by Linear Translation

Peter L. Donatelli

A few solutions exist that describe how a Linear Translation Multi-Axis (LTMA) polarizer can be made. It is the purpose here to describe some of these solutions and determine if these solutions are plausible. A positive result will be the creation of a LTMA polarizer in a continuous sheet.

As there are various ways to make a LTMA polarizer, there are also many materials used to make polarizers. Some of the types of polarizers that will be discussed consist of: a crystalline based dichroic polarizer, a molecular iodine polarizer, birefringent polarizers, metallic polarizers and light reactive dye polarizers.

What has resulted from the testing of some of these methods is the fabrication of a LTMA polarizer. The final product has accomplished the goals of attenuating light by linear translation, and multiple local transmission axes. It can be concluded that stress and temperature are crucial factors to successful creation of a LTMA polarizer.

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List of Symbols

Symbol	Description
<u>English</u>	
d:	Spacing between constructive interference patterns
LC:	Liquid Crystal
LCD:	Liquid Crystal Display
LLC:	Liquid Lyotropic Crystal
LTMA:	Linear Translation Multi-Axis
nm:	Nanometer
PET:	Polyethylene-terephthalate
psi:	Pounds per square inch
PVA:	Polyvinyl Alcohol
r:	Radius of circle
UV:	Ultra-violet
X:	Arbitrary number of degrees
x :	Coordinate on x-axis of circle
x_o :	Circle center, x-coordinate
y :	Coordinate on y-axis of circle
y_o :	Circle center, y-coordinate
<u>Greek</u>	
α :	Angle of incidence between light and normal to surface.
λ :	Wavelength of Light
μm :	Micron; micrometer
$\text{m}\mu$:	Nanometer
θ :	Angle between transmission axes of two crossed polarizers.
<u>Subscript</u>	
o:	Object
r:	Reference

Chapter 1: Introduction

Motivation

Over the past two decades there has been an increasing demand for a device that will reduce or eliminate unwanted glare from the rearview mirrors of automobiles caused by various sources such as the sun, or the headlights from a following car or truck.¹ A device that addresses this issue would enhance the driver's ability to see both during daylight and darkness, thus improving the vehicle's overall safety. Industry has answered this demand by creating various types of electrochromic and/or automatically dimmable mirrors. However, these devices often have a limited life span, especially those mounted externally, and are often costly to install and replace.

Approximately 58 million light vehicles are produced worldwide, annually. North America, Europe and Asia/Pacific regions each account for about 1/3 of that total.^{2,3,4} Of that 58 million, assuming the same relative percentages as above, approximately 41 million vehicles were registered, 13.8 million in the United States for 2003.⁵ Approximately 50% of the cars produced in 2003, worldwide, came equipped with dimmable mirrors.² It is estimated by the year 2009, there will be 68.7 million cars manufactured annually, a growing percentage of these projected to be equipped with dimmable mirrors.³

"Currently, there are about 732 million automobiles worldwide, 219 million in the United States" according to Frank Hampshire, Director of Research for AASA [1]. In 2003, an estimated 16% of all light vehicles (in use) worldwide were equipped with

¹ Gentex Corporation. Why NVS Mirrors [Automotive Section of Website]. Zeeland, Michigan: Gentex Corporation; c2004 [cited 2004 Aug. 6], [about 2 pages]. Available from: http://www.gentex.com/auto_why_nvs.html

² Gentex Corporation. Robust Technology, Value Added Features and Execution!. 2004. Presentation. Zeeland, MI: Gentex Corp.; 2004 Aug. 33p.

³ CSM | Worldwide [homepage on the Internet]. [cited 2004 Jul 30]. Available from: <http://www.csmauto.com/forecasts/>.

⁴ International Organization of Motor Vehicle Manufacturers [homepage on the Internet]. Paris, France: 2003 [cited 2004 Jul 30]. Available from: <http://www.oica.net/htdocs/Main.htm>

⁵ Auto Alliance [homepage on the Internet]. c2004 [cited 2004 Jul 30]. Available from: <http://www.autoalliance.org>

interior dimming mirrors, and 5% with exterior dimming mirrors.⁶ The remaining 615 million vehicles have standard, non-dimmable mirrors.

Currently, all motor vehicles have at least two mirrors, one being an exterior driver-side mirror and the other an interior rear view mirror, although, most vehicles come equipped with three mirrors, the third being an external, passenger-side mirror. This suggests a minimum of 1.2 billion, and up to 1.8 billion interior and exterior rearview mirrors combined, worldwide, which could use a multi-axis polarizer for mirror dimming.

Various mechanisms can be utilized to achieve dimmable mirrors. Gentex Corporation makes their dimmable mirrors by “sandwich[ing] an electrochromic gel between two pieces of glass, each of which has been treated with a transparent, electrically conductive coating, and one with a reflector”.⁷ These mirrors are then dimmable by applying an appropriate electrical signal.

Traditionally, cars have internal rearview mirrors that are of the prismatic, day-night adjustable type, and do not require any electronics to control them. They work by using a triangular prism with the thicker end towards the ceiling, and a reflective surface on the backside of the prism. When the mirror is flipped, the image is reflected from the front side of the prism, not the backside.⁸ External mirrors are simpler yet. They usually consist of a planar or convex mirror, depending upon which side of the car, a backing plate attached to an actuator (mechanical or electric to control position only), and a frame or housing. The convex mirrors do not have any type of anti-glare setting or dimming capability, which makes polarizers prime candidates.

⁶ Gentex, Presentation 15

⁷ Gentex Corporation. How NVS Mirrors Work [Automotive Section of Website]. Zeeland, Michigan: Gentex Corporation; c2004 [cited 2004 Aug. 6], [1 page]. Available from: http://www.gentex.com/auto_why_nvs.html

⁸ howstuffworks [homepage on the Internet]. [cited 2004 Aug 6]. Available from: <http://auto.howstuffworks.com/question20.htm>

These different types of mirrors, electrochromic or standard, interior or exterior, must meet certain safety requirements as set forth by the National Highway Traffic Safety Administration (NHTSA) [2]. Some of the requirements listed there, in no particular order, are:

- “All single reflectance mirrors shall have an average reflectance of at least 35 percent.”
- “If a mirror is capable of multiple reflectance levels, the minimum reflectance level in the day mode shall be at least 35 percent and the minimum reflectance level in the night mode shall be at least 4 percent.”
- “A multiple reflectance mirror shall either be equipped with a means for the driver to adjust the mirror to a reflectance level of at least 35 percent in the event of an electrical failure, or achieve such reflectance level automatically in the event of an electrical failure.”

Further stipulations regarding mirror mounting, mirror magnification, and radius of curvature for convex mirrors, can be referenced from the Department of Transportation Part 571: Federal Motor Vehicle Safety Standards, Subpart B, Standard No. 111: Rearview Mirrors [2].

A simple, purely opto-mechanical device, such as a multi-axis polarizer, that would allow the gradual dimming of the mirror within the prescribed ranges would be extremely useful especially where electrochromic mirrors fail. Such a device could be made robust enough to also be used on external mirrors of various shapes. Such “dimming” capabilities are not yet available through the rather fragile electro-chromic mirror technology, which is susceptible to UV radiation and freezing. Such a device would also benefit from being able to withstand the daily fatigue encountered by modern electrochromic mirrors as they are cycled through various changes in voltage, reflectance, and environmental effects.

Linear Polarizers

Many devices today make use of linearly polarized light; take for example, calculators, clocks, wristwatches and even sunglasses (polarized). These devices and many others take unpolarized light from sources such as light bulbs, the sun, and any other source that produces “natural” light and converts it into linearly polarized (p-state) light. Such a “transformation” is done through the use of a linear polarizer.

Natural light is said to be unpolarized, when in fact it is better to think of natural light as randomly polarized, or polarized in all directions. The light source emits photons in all directions and each photon is polarized in a different manner. “All emissions having the same frequency will combine to form a single resultant polarized wave [3].” This occurs for every differently oriented emission, of each respective frequency. So as the light source emits photons, various different polarization states exist throughout the entire realm of the emitted light.

As the natural light impinges upon the surface of a polarizer, the polarizer will “choose” to transmit a given orientation of the light and absorb all other directions. At any particular moment in time, the light impinging upon the surface of the polarizer can be broken into two orthogonal components, one being parallel to the polarization axis and the other perpendicular to the polarization axis of the polarizer (Figure 1.1). When the light impinges upon the polarizer, the polarizer will transmit one of those orthogonal states and block the other, depending upon what type of material is used in the polarizer.

One specific application where linear polarizers can be used is light attenuation. A pair of linear polarizers is set up such that one polarizer (called the analyzer) is behind the first with respect to the incoming light. Attenuation occurs by the polarizers crossing their respective polarization axes. The degree of attenuation is a function of the angle between the polarization axes. It is demonstrated by Malus’ Law, in Equation 1.1.

Figure 1.1: Unpolarized Light Impinging Upon a Linear Polarizer from *Optics*, by Hecht [3].

$$I(\theta) = I(0) \cos^2 \theta \quad (1.1)$$

In Equation 1.1, $I(0)$ is the initial irradiance of the light impinging on the first polarizer, and θ is the angle between the transmission axis of the polarizer and analyzer. When the two polarizers are perfectly aligned and their polarization axes are parallel, the angle θ is zero. As the analyzer rotates with respect to the polarizer, θ becomes larger until it reaches a maximum of 90 degrees and the two polarizers have transmission axes that are perpendicular to each other. At this point, no light is transmitted and maximum attenuation occurs (extinction). If the analyzer is rotated further, θ starts decreasing, and light is allowed to pass once again.

Multi-Axis Polarizers

A pair of multi-axis polarizers has certain advantages where a pair of conventional polarizers would not be suitable. For example, in conventional polarizers light attenuation occurs when one polarizer is rotated with respect to the other. In a situation where it is more feasible to slide the polarizers across one another as opposed to rotating them to attenuate light, a pair of multi-axis polarizers would be more useful.

Given a sheet of a linear polarizer, it should be noted that there is normally only one orientation to the polarization axis throughout the entire sheet. The purpose of a multi-axis polarizer is to give different local orientations of the polarization axis throughout a continuous sheet. If these local orientations of the polarization axes were arranged in a specific pattern (Figure 1.2 below), light could also be attenuated using these two “specially constructed” polarizers. The function used to generate this pattern is given in Equation 1.2:

$$y = \sqrt{r^2 - (x - x_o)^2} + y_o \quad (1.2)$$

Figure 1.2: Linear Translation, Multi-Axis Polarizer Pattern

The light emerging from the polarizers is p-state light, or linearly polarized light. The manner in which these polarizers would block the light again utilizes Malus’s Law from Equation 1.1, but the crossing of the polarization axes occurs from a pure linear translation of the two polarizers, as opposed to rotating one polarizer with respect to the other. Figure 1.3 demonstrates how attenuation is achieved by linearly sliding one Linear Translation Multi-Axis (LTMA) polarizer passed the other.

As the polarization axes cross and light attenuation occurs, it should be noted that the amount of linear translation is only a function of the radius of the circular pattern of the polarization axis. The larger the radius the more translation is needed for attenuation to occur. If the two sheets are slid past one another more than the radius of the pattern, the attenuation becomes less and less until the polarizers are again uncrossed. If more

than one pattern from Figure 1.2 is on a sheet, the attenuation will become cyclic as the two sheets are slid past one another. See Figure 1.3d, below.

Figure 1.3: Various stages of attenuation for LTMA polarizers. a.) Two uncrossed LTMA polarizers. b.) LTMA polarizers are crossed by $\pi/4$ radians or 1/2 the radius. c.) LTMA polarizers are fully crossed. The amount of translation is $\pi/2$ radians, which is equal to the radius of the pattern. d.) LTMA polarizers fully uncrossed. The translation equals the diameter of the pattern and the light attenuation will become cyclic.

Problem Statement

Linear polarizers have been around for quite some time, and as such, there are a variety of methods used to create them. There are processes that have been suggested to create a polarizer whose output is linearly polarized light and whose polarization axes are curvilinear. However, the closest things to date are discretized “patterned” polarizers, in which a pattern is formed in a sheet by piecing together areas of a linear polarizer. In creating a LTMA polarizer, the problem lies not in finding a pattern that may be used for the polarization axes, but manufacturing this polarizer with the specified polarization pattern in a smooth, continuous sheet. The purpose here is to demonstrate the concept and propose possible processes can actually be used to create a Linear Translation Multi-Axis polarizer. The outcome will be an actual physical working model.

Chapter 2: Review of Literature

Edwin H. Land was the first man to create a linear polarizer made from a sheet of dichroic crystals. The dichroic crystals he used are called herapathite, or are known chemically as quinine sulfate per-iodide. This sheet polarizer became and is widely known as the *Polaroid J-Sheet*. The *J-Sheet* polarizer was first made using a solution of herapathite crystals, which have a needle-like shape to them and then applying a magnetic field so the crystals would align in the same direction. Due to the size of the crystals the *J-Sheet* scattered light a bit and turned out to be hazy [3].

To prepare the crystals for the first polarizer, the crystals were “made by grinding herapathite crystals in a ball mill for a month; the mill contained a solution of nitrocellulose lacquer [4].” Once the crystals were ground small enough, the crystal solution was placed in a magnetic field. Before the field was applied, the crystals were randomly oriented in the solution and the solution was opaque and reddish black in color [4].” But when a field of about 10,000 gauss was applied, the crystals slowly began to align and the solution became transparent [4]. The crystal solution, still in the magnetic field, was examined with a Nicol prism, and the solution “went from white to black as the prism was turned [4].”

To create the *J-Sheet*, a sheet of plastic was dipped into the solution which was contained in a test tube, which was in the magnetic field [4]. The test tube was removed from the field, leaving a crystal coated plastic sheet behind [4]. As the sheet dried in the field, the crystals were still oriented parallel to one another and a sheet polarizer was made [4].

Once Land had created this first polarizer he tried different methods for aligning the crystals. Other methods include: 1.) An electric field, 2.) Stretching a sheet of rubber coated with a viscous colloidal crystal solution [11]. Although these methods provide fine linear polarizers, a better method was needed to produce mass quantities. Extrusion was the method decided upon. By extruding a sheet coated with a viscous crystal solution

through an extremely thin slit, the needle-like crystals “were oriented parallel to one another [4].” “This is the method employed in making the J polarizer [4].”

In making the *J-Sheet*, the size of the herapathite crystals is of particular importance. The crystals need to be small enough so as to lessen the amount of light scattered. The smaller the crystals are, the better the optical properties of the polarizer become. Crystals on the molecular level would be ideal, but this is very hard to achieve. Land later discovered the crystals he prepared for the *J-Sheet* were about one micron in length and merely fractions of a micron in diameter [4].

An evolutionary step in linear polarizers came in 1938 when Land developed the *Polaroid H-Sheet*. This type of polarizer is not made from dichroic crystals, but instead from a sheet of polyvinyl alcohol that is stretched in one direction and then dipped into a solution of iodine. The iodine attaches itself to the hydrocarbon molecules of the PVA, which are long chains, and the electrons of the iodine act as the conductors, moving along the chains like in a wire [3].

It is not clear from the reference how long the polyvinyl alcohol was soaked in the iodine solution, but varying degrees of the polarizer effectiveness occur as a result of the amount of iodine present in each polarizer, which was dependent of soak time. The different degrees of effectiveness are designated by names. For example, an ideal *H-Sheet* would be designated *HN-50* [3]. The H is for H-Sheet, the N is for neutral in color and 50 is the percent of light absorbed by the polarizer [3]. Some common commercially produced polarizers include: *HN-38*, *HN-32* and *HN-22* [3].

Land further discusses various types of polarizers in *Dichroism and Dichroic Polarizers* [5]. Of particular interest are the metallic polarizers. He states that: “When metallic salts are incorporated in oriented linear high polymers and are subsequently reduced to the metals, the product is often characterized by strong dichroism [5].” Land was much more concerned with quantitatively measuring the dichroism of the metallic

polarizers than explaining how they worked, in this article. He did however make reference to others' previous work with gold, silver, and mercury [5]. Land states:

The metallic particles are extremely small, widely separated rods oriented parallel to the cellulose fibers. Particle dimensions of the order of 10 mμ diameter, 100 mμ in length, are mentioned by Frey-Wyssling... Furthermore, in contrast to all the polarizers treated so far, the oriented absorbing particles here are not themselves dichroic, since every cubic crystal or liquid particle is of necessity an optically isotropic system [5].

The metal polarizers work, not because of dichroism, but because of their crystal structure. Silver is an optically isotropic crystal, which means it does not matter which way the crystals are oriented for them to absorb light. The chemicals used in black and white film are very similar if not identical to the chemicals (silver iodide) Land used to identify the shape and size of the herapathite crystals, and they also function as polarizers [4]. Secondly, when black and white film is exposed to light and then developed, the remaining product is pure silver, which is reduced from metallic salts.

Photographic film is made from a liquid dispersion of grains of silver halide salts in a gelatin matrix which is then laid on a substrate and allowed to harden [6]. This dispersion includes combinations of silver bromide, silver chloride, and silver iodide for various different grain shapes and sizes [6]. The grains are on the order of sub-micron size, depending upon how many crystals are in each grain [6]. The silver bromide and silver chloride can be used in combination with each other or separately, but silver iodide is always used in combination with one of the other two silver halides [7]. These silver halides are then treated with spectral sensitizers that allow the light energy from a photon to be transferred to the grain via a photo-electron [6]. As the production of black and white film has evolved, the silver halide grains have become flattened out to produce more light capturing surface area than the cubic grains in which the salts are normally found, which reduces the cost of the film [7].

To produce an image, the film is exposed for a relatively short period of time (on the order of thousandths of a second) to light [6], which causes a photochemical reaction in the silver halides. The light impinges upon the treated silver halide crystal causing the anion of the salt (Br^- , Cl^- , or I^-) to free an electron. The electron then attaches itself to

the cation (Ag^+) producing a pure, neutral silver atom. It is believed that only four silver atoms are needed in a grain to produce a stable latent image [6]. The longer the exposure time to the light, the more silver atoms are produced per grain.

Once the image is captured, it must be developed. To develop the film, it is placed in a developing solution, which acts as a reducing agent [6]. The developer reduces the silver ions to silver atoms [6] and oxidizes the anions of the silver halides. The grains that have latent images develop faster than those without [6]. Eventually, if the film is left in the developer long enough, all silver ions will become silver atoms [6]. Once the image is developed, the next step is to stop the developing process, so the film does not become over developed [7]. This is usually done by placing it in a weak acid solution called a stop bath for a few seconds [7].

To fix the image, all leftover silver halides that were not developed must be removed from the film [7]. As it turns out, silver halides are only slightly soluble in water. Therefore, a solution of sodium thiosulfate is used to “dissolve” the silver halides and leave the silver atoms behind, thus giving a permanent image [7].

Black and white film would be ideal to create a LTMA polarizer. The film would be exposed to the pattern of the transmission axes and developed. The silver left behind in the film would polarize light in the desired pattern. This process however is messy due to the use of chemicals for developing the film. A “dry” patterning procedure, using no chemicals would be more efficient.

An article entitled *A New Conductor Structure for Plastic LCD Applications Utilizing ‘All Dry’ Digital Laser Patterning* describes a new structure and procedure for construction of the conducting layer in a liquid crystal display (LCD) [8]. The conducting layer is composed of five thin-film sub layers [8]. With the conductive layer constructed, it can then be digitally patterned using laser light. It should be noted that this conductive layer has a “high optical transmission (>83%), while maintaining absorption at the 1100 nm laser wavelength for ablation patterning [8].” The laser that is used to pattern the

electrodes is a Polaroid 9000T fiber laser, which can be found in laser printers, which makes for easier mass production [8]. The laser can go as small as 10 μm in diameter for patterning and no photo-mask is needed [8]. Any modifications to a pattern can be obtained by “simply modifying a digital image file [8].” Patterning of the electrodes is accomplished by ablation of the conductive material [8].

As the previous article describes a method of patterning using light, so does the article entitled *Photo-Patterned e-wave Polarizer* [9]. The article explains two manufacturing processes for an e-wave polarizer that will allow different local directions of the polarization axes.

The first method discussed is a “reverse transfer” method of using photo-curing glue to transfer a polarizing film onto a substrate using a Liquid Lyotropic Crystal (LLC) solution. Basically, a UV curable photo-resist is cast onto a glass substrate. A polarizing film is then laid over the photo-resist [9]. Then, using a photo-mask, UV light the exposes certain areas of the photo-resist curing and hardening it [9]. Any unexposed areas are washed away by a solvent, the polarizing film is removed from the unexposed areas, and the process is repeated for as many different polarization “vectors” as desired.

This process will allow a continuous sheet polarizer to have different local orientations of the polarizing axes, which is very desirable. This process though, seems to take discrete pieces of a linear polarizer to make a “continuous” polarizer with different local orientations. This means that the new “multi-axis” polarizer will only be as fine as the pieces of linear polarizer were that were used to make it.

The second method discussed for a multi-axis polarizer is the “photo-alignment method” which uses LLC’s [9]. A light reactive dye, specifically, an azodye, AD-1 is spin coated onto a substrate [9]. The thickness of the dye layer is about 100 nm [9]. A shadow mask is projected onto the dye, and is cured using polarized UV light [9]. The dye aligns along the polarization axis of the UV light. Once this “photo-alignment layer” is made, a “few drops of an isotropic LLC solution are dispersed” onto it [9]. As the

liquid crystals solution evaporates, the crystals are left behind and are oriented “preferentially along the photo-induced axis, where the absorption axis of the LLC is parallel to that of the photo-alignment layer [9].”

This method makes use of polarized light to cause a photo-chromic reaction in the dye layer to align the dye molecules in a specified direction. A LLC (Liquid Lyotropic Crystal) solution is then dispersed onto the dye layer. As the solution evaporates, the azodye anchors the LLC's and the liquid crystals are oriented parallel with the dye layer. The combination of the dye and LLC's are what cause the polarization of the light passing through them.

Summary

There have been a variety of different types of polarizers discussed in this chapter. They range from miniscule dichroic crystals to submicroscopic metal slivers to light reactive molecular dyes. The key ideas that can be obtained from this chapter that are important factors for polarizers are: particle size and orientation of these particles.

Chapter 3: Patent Review

There are various ways to create different types of polarizers. Many of these types of polarizers and the methods used to create them have been patented. This chapter will summarize some key ideas that have been patented which were used to create linear polarizers in the hopes that it is possible to modify some of these ideas to create a LTMA polarizer.

Patent 3,235,631: Polarization Process

This patent describes and explains a process for creating a discretized multi-axis polarizer in a continuous sheet. The dichromophore in this patent is iodine, bonded to a long chain polymer such as polyvinyl alcohol. The desired discretized patterns are transferred onto the substrate by inducing localized stresses in the substrate using a rotating drum or a stamp and dye combination, having the desired patterns scribed into them.

In order for this polarizer to be effective as a discrete type “patterned” polarizer, the molecules the iodine is attached to must follow the prescribed pattern. To accomplish this, a rotating drum or a reciprocating stamp must first be scribed with the desired pattern. This patent makes reference to several “known” procedures of inscription. Then a mixture of polyvinyl alcohol and iodine is applied to a substrate and allowed to dry. At this point, the molecules are randomly oriented. Next, the inscribed drum, with several local patterns, passes over and applies pressure to a substrate [10]. The pressure applied to the substrate and PVA mixture via the inscribed drum or stamp reorients the molecules along the stress lines that were induced [10].

Patent 3,437,401: Light-Intercepting Sheet for an Illuminated Display Device

This patent uses a “patterned” polarizer for signage applications, and is very similar to the previously mentioned patent. However, the method of production of the polarizer is slightly different, as per the use of birefringent materials.

This patent also makes use of an embossing plate to generate an embossed pattern on either a transparent sheet of plastic or a birefringent material. The embossing plate is used to generate local stresses in the substrate. If the substrate is an isotropic material, a molecular realignment occurs, and the molecules do not follow the induced stress lines, but are in fact, perpendicular to them [11]. However if the stressed material is birefringent, the molecules realign themselves along the induced stress lines [11].

The birefringent substrates suggested in this patent are vinyl acetate, cast acetate, Tenite acetate, also known as Tenite, or any other acetate-butyrate plastic sheet [11]. An excerpt from the patent best explains the phenomenon of forced birefringence:

This phenomenon may be termed forced birefringency since it is believed that the pressure of the embossing operation causes the molecular structure of the material to undergo localized reorientation along the stress lines in the material created by the force applied to form the embossed lines. This causes double refraction in an isotropic material along controlled lines so that it in effect exhibits birefringence. Of course if the sheet is made from birefringent material, the already existing lines of stress will be directionally reoriented by the embossing operation [11].

To effectively emboss the substrate, certain conditions are preferred. It is desired to have the embossing plate at an elevated temperature, yet below the melting point of the substrate, and the pressure applied to the substrate be less than the “flexural strength of the sheet material” [11]. The conditions suggested in this patent are a sheet of Tenite, 10 mils thick, or .01 inches, at a temperature of 250 °C to 275 °C and a pressure between 6,000 and 10,000 pounds per square inch (psi) [11]. It should be noted that the temperatures and pressures vary for different materials.

To create the embossing plate, a photoengraving process is suggested. Virtually any pattern that can be drawn can be put onto the embossing plate. This pattern is then photographed and the negative is used for photoengraving [11]. If the picture is larger than needed, a photo-reduction of the image can be done and more lines can be engraved onto the plate [11].

As for the spacing of the pattern lines for the embossing sheet, there need not be as many as one would think. “In practice about fifty embossed lines per inch are commonly employed with good results [11].”

This patent also suggests the use of polyvinyl alcohol and “polarizing ink” to animate signs. The polyvinyl alcohol and “polarizing ink” for this patent both come from the Polaroid Corporation under the names *Vectograph* or *H-Sheet* for the PVA and *Vectograph Ink* or *H-ink* for the polarizing ink [11].

In the application of backlit signs, the *Vectograph* PVA is laminated to a sheet of Tenite, and the desired motion pattern is embossed on the face of the Tenite opposite the *Vectograph* [11]. The polarizing ink is then applied to the Vectograph over the embossed areas [11]. Conversely, a pre-inked Vectograph can be applied to the Tenite and then the Tenite is embossed [11]. Areas of unwanted motion may be depolarized using a saturated solution of sodium phosphate [11].

Patent 3,941,901: Surface Alignment Method for Liquid Crystal Cells and Production of Polarizers Therefor

This patent is in the area of LCD displays, in particular the method of aligning the liquid crystals on the surface of the cell. Previous techniques, such as rubbing the cell wall with cotton, paper, or a buffing wheel, or evaporating silicon oxide onto the cell wall employ the use of microgrooves to align the liquid crystals. This patent explains a method that is easier and less expensive. Using a technique known as shear thinning, an elongation in the direction of the shear force induced into a polymer in order to align the long chain like molecules occurs due to a reversible decrease in viscosity from an applied shear force [12].

A long chain polymer such as polyvinyl alcohol, PVA, is applied to a substrate in liquid form. Before the polymer dries, a squeegee slides across the substrate and PVA, spreading the PVA evenly across the substrate. In the process, the long molecules of the PVA will become aligned in the direction the squeegee moved. After the PVA has dried,

the molecular orientation is preserved. When the liquid crystals for the display are introduced to the cured PVA, they will align themselves in the direction of the stretched PVA molecules [12].

If a dichromophore such as iodine is introduced to the PVA before it is cured, or even after it has cured, the PVA and iodine will act as a polarizer even when the liquid crystals are added [12]. This would eliminate the need for external polarizers for LCD displays.

Patent 4,049,944: Process for Fabricating Small Geometry Semiconductive Devices Including Integrated Components

This patent pertains to processes for making patterns for sub-micron sized semiconductors. A photoresist layer and ion beam etching are employed; however it is the exposure of the photoresist which is considerably different. To create the desired pattern on the semiconductor device, the photoresist is exposed using optical interference patterns [13]. This will allow the patterns to become much smaller than previously attainable. This process may also be used to create metal grid type polarizers [13].

To begin, a photoresist layer, such as Kodak corporation's metal etch negative resist (KMER) or their thin film negative resist (KTFR) as mentioned in the patent, is deposited on a suitable substrate [13]. It should be noted that a positive photoresist can also be used. After the photoresist has dried, it is exposed to an interference pattern made from a pair of coherent, (900 nm) laser beams [13]. The laser beams interfere with each other, both constructively and destructively, and produce interference fringes. The spacing (center to center) between two consecutive light spots and two consecutive dark spots from the interference pattern, respectively, is given by [13]:

$$d = \frac{\lambda}{2} \sin \alpha \quad (3.1)$$

Here d is the distance between the light areas (center to center), λ is the wavelength of the laser light, and α is the angle of the laser, from the normal of the surface of the substrate

[13]. The light from the laser will harden the area of the photoresist exposed to the interference pattern, and the unexposed areas can be washed away by a developing solution. This practice of exposing and developing is well known in the industry and is taken as common knowledge. An argon ion beam is then used to remove material in the substrate between the areas of hardened photoresist [13].

This patent describes several applications for this small geometry structure, but the one of most interest is for making a wire grid polarizer. To obtain a wire grid polarizer, a thin layer of metal such as gold or silver is sputtered onto the substrate before the photoresist is added. The spacing between the metal ribs should be between 0.1 μm and 0.4 μm [13]. This would make a wire grid polarize for the visible portion of the spectrum. If these wires are formed in the shape of the pattern in Figure 1.2, a suitable LTMA polarizer could be made from a wire grid.

Patent 4,166,871: Iodine Stained Light Polarizers

This patent in general, describes a process for making a PVA-iodine polarizer for the visible region. The purpose is to decrease the amount of light leakage in the extreme ends of the visible spectrum (red and blue regions). Stretching operations are performed on the PVA, but what are of particular interest, are the solutions that are used for the polarizing ink.

The solution the stretched PVA is dipped into consists of iodine, potassium iodide, and water, in the ratios of 1/15.82/328 by weight [14]. The soaking occurs at about 35 °C for about 15 seconds [14]. Once the PVA sheet is treated with the iodine solution, it is then “fixed”. This fixing solution consists of potassium iodide, boric acid, zinc chloride and water in the ratios of 1.95/1.25/1.0/25.67 by weight [14]. The fixing occurs at about 74 °C for about 25 – 30 seconds [14]. If the iodine impregnated PVA is not treated in the fixing solution, “much of the active iodine is removed” during subsequent processing [14]. It is the boric acid which stabilizes the iodine, and it also adds heat and moisture stability [14].

Patent 4,514,479: Method of Making Near Infrared Polarizers

This patent describes a four step process for making wire grid type polarizers for the near infrared region of the spectrum. Basically, a conductive layer is cast onto a substrate, and then a layer of photo-resist is cast over the conductive layer to protect it [15]. The photoresist is then exposed to an interference pattern from two beams of a laser and the unexposed photo-resist is washed away by developing [15]. This produces a surface grating in the photo-resist [15]. This surface grating is then milled away by ion milling to reproduce the surface grating in the conductive layer [15].

The key idea in this patent is the use of interference patterns produced by two coherent lasers. The laser beams interfere with each other both constructively and destructively and expose a particular pattern (straight lines in this case) in the photoresist. The fringe spacing is given by [15]:

$$d = \frac{\lambda}{(\sin \theta_o + \sin \theta_r)} \quad (3.2)$$

Here, λ is the wavelength of the laser, $\theta_{o,r}$ are the angle of incidence of object and reference waves measured in the material, respectively [15].

Patent 4,591,512: Method of Making Light Polarizer

This patent is very similar to the previous patent, 4,166,871, in that it also provides a method for creating a linear polarizer from a PVA and iodine mixture. Again, the PVA is linearly stretched, and the iodine dye used has the same composition, but in different concentrations. This patent gives the concentrations of iodine, potassium iodide, and water for the ink solution in the ratios of 1/237/3727 by weight, respectively [16]. For the borating solution, the ratios of potassium iodide, boric acid, zinc chloride, and water are 1.02/1.25/1.0/26.49 by weight, respectively [16].

The soak times and temperatures are also different. Here, the PVA is soaked in the iodine solution for about 2.3 minutes to 5.4 minutes at 55 °C – 66 °C, depending upon how fast the sheet moves through the solution, and in the borating solution for 3.4 minutes at 60 °C [16].

Patent 6,122,103: Broadband Wire Grid Polarizer for the Visible Spectrum

Wire-grid polarizers are commonly used for polarizing electromagnetic waves in the infrared region of the spectrum. This patent describes a metallic wire-grid type polarizer for the visible spectrum, where the “wires” are not actually wires, but metallic ribs.

Center to center spacing of the wires is the key factor that determines what part of the spectrum the grid will polarize [17]. From the patent:

If the grid spacing or period is long compared to the wavelength, the grid functions as a diffraction grating, rather than as a polarizer, and diffracts both polarizations (not necessarily with equal efficiency) according to well known principles. When the grid spacing or period is much shorter than the wavelength, the grid functions as a polarizer that reflects electromagnetic radiation polarized parallel to the grid elements, and transmits radiation of the orthogonal polarization [17].

The grid in this patent uses aluminum as the conducting metal for the ribs and has dimensions given by: center to center spacing or “period $p = 0.2 \mu\text{m}$, conductor width $w = 0.1 \mu\text{m}$, conductor thickness $t = 0.1 \mu\text{m}$, and substrate refractive index $n = 1.525$ ” [17]. The length of the ribs should be larger than the wavelength of the light they are trying to polarize [17]. For the visible region, the ribs should be at least 700 nm long, but they may be longer.

Methods that describe the process for creating the metallic ribs are not of critical importance for this patent. References are made to Patent 4,049,944 for ion beam etching and high resolution lithography techniques to create the metallic ribs.

Patent 6,630,289: Photo-Patterned Light Polarizing Films

This patent pertains to the use of light reactive dyes and liquid lyotropic crystals to create a “patterned” polarizer for LCD applications. These “patterned” polarizers are actually pixilated polarizers, with each pixel having a different transmission axis than the adjacent pixel [18].

To create such a polarizer, a light reactive dye, such as an azodye, AD-1, is coated onto a rigid or flexible substrate [18]. The thickness of the azodye layer may range from 50 nm to 1.5 μm thick [18]. Sections of the azodye are then exposed to polarized UV light or a certain orientation, causing a photo-chromic reaction in the dye layer to align the dye molecules in a specified direction. An LLC solution is then dispersed onto the dye layer. As the solution evaporates, the azodye anchors the LLCs and the liquid crystals are oriented parallel with the dye layer. The critical factor for this process is the evaporation rate of the solvent used in the LLC solution [18]. If it is evaporated too fast, the solution “boils” which ruins the polarizer, whereas too slow an evaporation rate causes random orientation of the molecules [18].

The combination of the dye and LLCs are what cause the polarization of the light passing through. This process is repeated until all desired different orientations of the transmission axis are obtained.

Summary

There have been a variety of different patents presented in this chapter which were reviewed because they present methods to create linear polarizers. These methods range from simple operations such as stretching PVA and dipping it into an iodine bath to more complex methods such as exposing photoresist with nano-scale interference patterns, followed by ion etching of the exposure. These methods are good for creating linear polarizers and with some modifications to these processes, they should make LTMA polarizers with good results as well.

Chapter 4: Technical Discussion and Methodology

This chapter will describe several different possible methods for creating the polarizing pattern, and the type of polarizer for which that process works best. First will be a method to prove the concept of a LTMA polarizer. All other methods propose variations to different existing fabrication methods for linear polarizers in order to make a LTMA polarizer. What follows is a detailed description of the proof of concept, followed by types of polarizers that may be used for an LTMA and the procedures that may be used to make them.

Proof of Concept

It is a good idea to first make sure the concept of having different local transmission axes works for an LTMA polarizer. To demonstrate the concept, a sheet of ordinary linear polarizer will be used. The linear polarizer will be cut into $\frac{1}{16}$ th inch strips such that each strip will have its transmission axes progressively rotated five degrees from the transmission axis of the previous strip. Once the strips are cut, they will be arranged so their transmission axes are aligned as in Figure 4.1.

Figure 4.1: Discrete LTMA polarizer with transmission axes progressively rotated five degrees from the previous strip.

The following types of polarizers are suggested methods for creating an LTMA in a continuous sheet.

Type 1: Dichroic Crystal Polarizer

Based on the previous work of Land, a linear polarizer can be constructed using dichroic crystals of various types (tourmaline, herapathite, silver iodide, etc.). Land created his polarizer, the J-Sheet, by linearly stretching a substrate which had a solution of dichroic (herapathite) crystals laminated on it [3]. This linear stretching aligned the crystals along their optical axis, which happened to be the same as their longitudinal axis. In order to create a multi-axis polarizer using dichroic crystals, there must be a method of aligning the crystals in the desired pattern as illustrated by Figure 1.2, as this represents the desired transmission pattern.

Method 1: Nanochannels

The crystals Land used have a needle-like shape with a length-to-width ratio of about 10 [3]. To reduce the amount of light that was scattered, the crystals were on the order of 1 micron long by about 100 nm in diameter [4]. For herapathite crystals, the transmission axis, or optical axis, is the same as the major axis of the crystal, so having the crystals settle in curved channels or grooves will allow the crystals to orient themselves so their transmission axis is along the grooves. This will be possible because a circle can be thought of as an infinite number of straight line segments, and the radius of the circle is large enough to allow a 1 μm long by 100 nm wide crystal to fit into a “curved” channel.

A sheet of optically clear plastic will be used as a substrate for the polarizer. This sheet will then have sub-microscopic curvilinear channels cut into it. These nano-channels will be approximately the width of one dichroic crystal (100 nm). The cross-sectional shape of the channels can be square or circular with a consistent depth not less than 50% the diameter of the dichroic crystals and not more than 95% the diameter of the

crystals. The overall pattern of the channels is shown in Figure 1.2 with a radius dependent upon the amount of linear translation allowed or other such limiting specifications.

The channels can be cut by various methods, preferably whichever is fastest and of least cost. Striking the substrate with a stamp of the patterned channels is one possible method. This is a common method used by mints to create holographic images on coins. Other such methods are mentioned in U.S. patent 6,122,103. These methods apply holographic interference lithography to form the fine spacing of the channels followed by ion beam etching or e-beam lithography to create the pattern followed by ion etching [17]. Once the pattern is imprinted into the substrate, the dichroic crystals are broadcast onto the engraved substrate in powder form.

As the dry crystals are spread onto the substrate, some will align themselves with the nano-channels and fall into them. Other crystals will lie above the channels. To ensure all the crystals are properly seated in the nano-channels, a gentle random shaking of the substrate, in the plane of the substrate, will allow any crystal not already in a channel to fall into one. Any excess dichroic crystals can be gently removed from the substrate and recycled for future applications. Once all excess crystals are removed, a second optically clear, adhesive treated, uncut substrate is applied. The second substrate can be used to laminate the crystals in place and provide a protective coating, or it can be removed, thus removing the crystals with it. The adhesive would ensure the crystals stay in place; however, they would be susceptible to smearing because they would be exposed to the environment. The simple touch of a finger to the exposed surface would misalign the crystals at that site, ruining the polarization.

Method 2: Centrifugal Force

Another manner to align dichroic crystals in the nano-channels involves a viscous solution similar to Land's. If this solution is applied to the patterned substrate, the crystals can be aligned by subjecting the substrate to a centrifugal force. As the substrate

is spun, the crystals will be forced into the channels and become aligned with the channels. At the same time, any excess solution will be forced from the sheet. The solution can then be allowed to dry and the patterned crystals may be transferred.

Method 3: Shear Force

When Land decided to mass-produce the J-Sheet, he used a viscous solution of herapathite crystals. This solution was then extruded through a very long and extremely narrow slit. Once the sheet of viscous solution passed through the slit, the crystals in the solution became aligned, parallel, along their long axis, which happened to be the transmission axis. To create a LTMA polarizer, the same principle can be applied, except the sheet needs to be extruded in two directions.

A sheet of substrate is secured to a flat level surface. A solution of the dichroic crystals is then applied to the substrate. Then, a “polarizing squeegee” is passed over the substrate along the prescribed pattern, shearing the viscous solution of herapathite crystals. The crystals will align themselves along the direction of shearing. The process is repeated until a suitable product is created. This will ensure virtually all of the crystals are aligned so that their transmission axis is parallel to the specified polarization pattern.

Type 2: Iodine Polarizer

Review

In 1938 Land created a new type of polarizer that worked without the use of dichroic crystals. He called it the H-Sheet and it was made from polyvinyl alcohol that was heated and stretched in one direction (to align the molecules linearly) and then dipped into an iodine rich solution. This allowed the iodine atoms to attach themselves to the long chainlike molecules of the polymer.

This polarizer works on the molecular level and is analogous to a wire-grid polarizer. When light impinges upon the polarizer, the component of the electric field

parallel to the long molecular chains excites the iodine, driving its electrons along the molecular chain, and is absorbed [3]. The component of the electric field perpendicular to the molecular chains is allowed to pass, making the transmission axis of the polarizer perpendicular to the orientation of the long polymer chains.

Another polyvinyl alcohol based polarizer is known as the *K* polarizer. It is made also by stretching polyvinyl alcohol, but then the polyvinyl alcohol is partially dehydrated, leaving behind polyvinylene. The polyvinylene is the dichromophore in this polarizer, not iodine.

Method 1: Squeegee Application

To make a LTMA polarizer, the same principals for polarization will be used; the difference though, is the way in which the polyvinyl alcohol is stretched. The PVA will be stretched in a curvilinear manner, not a linear fashion. This has not previously been performed.

The curvilinear stretching comes from applying the PVA to an optically clear substrate in a semi-circular manner. This is accomplished by spreading the PVA with a straight edge (polarizing squeegee) along a controlled path so that the polymer chains align themselves in the direction of shearing. This is analogous to Land's extrusion of the *J Sheet* through a very narrow slit, the slit in this case moving in two directions as opposed to one.

The path the polarizing squeegee takes is of critical importance. Holding one end of the squeegee stationary and allowing the other end to trace the desired path will create only a rainbow pattern. This will not produce the necessary pattern. If however, the squeegee is held at a constant "vertical" position while the pattern is traced using a "horizontal" motion, this will yield the desired polarization pattern. See Figure 4.2 below for a better depiction.

Figure 4.2: Squeegee remains vertical while tracing a semi-circular path in the PVA.

Once the PVA is applied to the substrate in the desired pattern, the appropriate dichromophore can be used.

Type 3: Stressed Induced Birefringent Sheet

Stress induced or “mechanical” birefringence, also known as photoelasticity, is not a new phenomenon. It has been around since Brewster discovered that “normally transparent isotropic substances could be made optically anisotropic by the application of mechanical stress,” in 1816 [3]. Photoelasticity has a wide range of applications, one of the most notable being the analysis of stress in an object, either transparent or opaque. As force is applied to an object, internal stresses occur, and when viewed between a pair of crossed polarizers, black bands of constant stress can be seen [3].

Method 1: Embossing

Stress induced birefringence could be especially useful in creating a LTMA polarizer. A plate, considerably harder than the substrate to be used, would have an array of the pattern in Figure 1.2 etched on it. The etched plate would then impact the substrate

leaving an imprint of the pattern from the plate. Along with the newly created pattern would be lines of stress from the “embossing” operation. According to Patent 3,437,401:

When the aforementioned embossing plate is pressed against a sheet of isotropic material to emboss the lines thereon, the molecular structure of the sheet undergoes a localized orientation along the small invisible stress lines in the sheets generally perpendicular to the embossed lines. When sheets of birefringent material are embossed, the existing molecular orientation is changed and the molecules are directionally reoriented along the aforementioned stress lines created by the embossing operation [11].

So by embossing the birefringent material with the pattern in Figure 1.2, the local lines of stress are orthogonal to the embossed lines of the pattern. This does not create a problem however because it effectively creates a phase shift in the pattern to the left or right by $\pi/4$ radians or equivalently, the radius of the semi-circle.

The important part of this operation is to ensure that the frequency of the light that impinges upon the polarizer lies within the absorption band of the stressed birefringent material in one direction, and outside the absorption band of the stressed material for the opposite direction. This ensures that light of one polarization will be absorbed by the material and light of the orthogonal polarization will be allowed to pass through. This makes the stressed material dichroic.

It should also be noted that a polarizing ink may be applied to the sheets either before or after the embossing operation [11]. The molecules of the polarizing ink will then align themselves along the stress lines in the embossed sheet.

Method 2: Rolling

Another method to induce stress into the substrate resembles a rolling operation for thinning sheet metal. The sheet metal is passed through a set of rollers (parallel along their rotating axes). As it passes through, stress is imparted to the sheet in the direction of rolling, thus thinning and elongating the metal.

Similarly, if the sheet metal were replaced by a suitable birefringent substrate for a polarizer, such as Tenite, stress would be imparted into the substrate in the direction of rolling. Now, to obtain the desired polarizing pattern, as in Figure 1.2 or any multiple thereof, one of the rollers remains stationary while the other roller oscillates back and forth along its longitudinal axis while the substrate passes through. In Figure 4.3 below, the bottom roller is the one that oscillates along its long axis.

Figure 4.3: Bottom roller oscillates while rolling ink onto the substrate to produce desired stress pattern.

This operation may present a problem of tearing the plastic substrate. To remedy this, the oscillatory roller should be lubricated against the sheet. The lubrication however, must not interfere with application of a polarizing ink, which is why using the polarizing ink as lubrication is suggested. Care must be taken not to damage the polarizing ink by applying too much pressure or heat in the rolling process.

Type 4: Metallic Polarizer

Metallic polarizers work, not because of their dichroism, but the fact the metal crystals are optically isotropic. One specific metal used for polarizers is silver, although others metals such as aluminum, gold, and mercury have also been used, with their particle size on the order of 100 nm long by 10 nm in diameter [5].

Method 1: Black and White Photographic Film

Silver is one of the main materials used in black and white (B&W) photography. A photochemical process such as B&W photography would be an ideal method to make a multi-axis polarizer. The idea here is to expose a piece of black and white film to a pattern that will leave behind the desired pattern for a linear translation multi-axis polarizer when the film is developed, namely the pattern in Figure 1.2. This, in turn, will create a curvilinear metallic grid polarizer.

Exposure of the film to ordinary unpolarized white light would be ideal as this type of light is readily available at little or no cost. The only problem with this process is that a photo-mask must be used to cover the areas where the silver wires are desired so when the light exposes the film, silver atoms are left behind to form the wires. Photo-reducing processes are available, but it is uncertain if the pattern can be reduced small enough to have the correct width and spacing between the wires. The wires of the grid must be spaced apart (center to center of the wire) at least one half the wavelength of the shortest wavelength of light to be polarized for the grid to act as a polarizer, otherwise the grid will act as a diffraction grating [17].

An alternative to using a photo-mask would be to use an interference pattern generated by two or more coherent light sources such as lasers.

Method 2: Etching

Instead of using black and white film, another method to create a LTMA wire grid polarizer would be to simply etch away the unwanted areas from a substrate covered in silver, or other isotropic metal.

After having deposited a thin layer of silver (approximately 100 nm thick as per Patent 6,122,103) on a substrate such as glass, a layer of photoresist is applied on top of the metal [24]. Then using interference of two coherent light sources (i.e. laser light), the photoresist is exposed to the pattern in Figure 1.2 by moving the substrate in a semi-circular manner, at a predetermined diameter while the interference pattern is focused at one stationary spot. See Figure 4.4 below. The constructive interference “dots” from the laser will be spaced apart by the following equation [13]:

$$d = \frac{\lambda}{2} \sin \alpha \quad (4.1)$$

Here d is the distance between the light areas (center to center), λ is the wavelength of the laser, and α is the angle of the laser, from the normal of the surface of the substrate [13]. The light from the laser will harden the area of the photoresist exposed to the interference pattern, protecting the metal underneath, and the unexposed areas can be washed away by a developing solution. Once the photoresist is developed, the metal layer may be etched using ion beam lithography.

Figure 4.4: Interference Pattern from two coherent light sources. The photoresist coated substrate moves underneath the interference pattern to produce the desired pattern.

Type 5: Liquid Lyotropic Crystals and Light Reactive Dyes

Method 1: Discrete Photo-Patterned Polarizer

In mathematics, any smooth curved line segment can be approximated by a series of straight lines. Approximating functions and curves by summing small pieces is the basis for calculus and several numerical approximation methods. As the line segments become smaller, the approximated curve becomes smoother and smoother. If the line segments are fine enough, any difference between the actual curve and the approximated straight line curve becomes imperceptible. This method has also been employed in printing methods.

Another way to create a continuous sheet LTMA polarizer may come from an approximation of the continuous pattern in the form of a series of individual “discrete” linear polarizers, much like the proof of concept. These discrete linear polarizers would be in the form of thin (width-wise) strips, with each strip having its transmission axis rotated X degrees from the longitudinal axis of the strip. This can be better visualized in

Figure 4.1. The width of the strip and the amount of degrees the transmission axis varies from the longitudinal axis of the strip depends on how fine the LTMA is desired to be.

An article entitled, Photo-Patterned e-Wave Polarizer describes a discrete process for creating a polarizer for liquid crystal displays. The use of photo-curing glue is the key to this operation. Basically, photo-resist is cast onto a suitable substrate such as glass. Linear polarizing material is then laid over the photo-resist. UV light is then projected onto the areas of the photo-resist that are to be cured [9]. Once the photo-resist is cured, the undeveloped photo-resist is washed away by a developing process [9]. This process is then repeated for each desired area of different polarization.

If the discrete pieces of polarizer are set up so that their transmission axes create the pattern in Figure 4.1, this would make a great LTMA. Problems may arise from the glass substrate, due to its fragile nature and also the width of the strips of polarizer. They must be small enough so the human eye cannot detect that the continuous sheet is a series of discrete polarizers when two LTMA's are slid past one another. Special care must also be taken with the strips so that no light leaks between them at the seams.

Method 2: Photo-Patterned Polarizer

Liquid crystal displays need polarizers to work. Typically a linear polarizer is mounted on the exterior surface of both the front and rear of the LCD. On the interior lies a liquid crystal layer and an alignment layer so the liquid crystals are oriented parallel with the polarizers on each side.

This method makes use of specifically oriented polarized light to cause a photochromic (temporary) or photochemical (permanent) reaction in a photo-sensitive dye to align the dye molecules in a specified direction. Once the dye molecules are aligned in the specified direction, a LLC solution is then dispersed onto the dye layer [9]. As the solution evaporates, the azodye anchors the LLC's and the liquid crystals are oriented parallel with the dye layer [9]. It is a combination of the dye and the LLC which

polarizes the impinging unpolarized light. Virtually any pattern that can be thought of can be made into a polarizer using this method. A shadow mask blocks out the unwanted portions of the pattern so they are not exposed to the polarized UV light. One thing that must be changed however is the polarization of the UV light.

To make the LTMA with this method, the azodye layer would be laid down on the substrate [9]. Once the azodye is prepared, a polarized UV light would trace out the figure of a semi-circle with predetermined dimensions. As the UV light traces the pattern, the polarization axis of the UV light rotates so the molecules will have an orientation as in Figure 4.5. Note that Figure 4.5 does not represent a pattern to be made into a polarizer, but the orientation of the polarization axis in the polarizer.

Figure 4.5: Polarized ultraviolet light sets a photo-curing dye as it moves in the desired path. The polarization of the light rotates as it traces out the pattern.

Summary

Five different types of polarizers were introduced in this chapter. There are a variety of methods presented to create each type, some very simplistic while other methods are more complex, and may require industrial equipment. With modifications to methods presented in the two previous chapters, it is believed that the methods presented in this chapter will become viable solutions to the problem of creating a LTMA polarizer. The iodine and dichroic crystal polarizer types will be further explored.

Chapter 5: Results

This chapter will describe the results of various attempts to create a LTMA polarizer. Not every type of polarizer, nor every method described in Chapter 4 was tried, due to constraints on both time and money.

Proof of Concept

To prove the pattern in Figure 1.2 works for creating an LTMA polarizer, a working model was needed. A sheet of *HN-38* polarizing film was obtained from polarization.com. The sheet was cut into 1/16th inch wide strips such that the transmission axis of each strip was progressively rotated five degrees from the transmission axis of the previous strip. When the strips were arranged and secured with Duck brand clear packing tape, a LTMA polarizer resulted. This can be seen in Figure 5.1 below.

Figure 5.1: Discrete LTMA polarizers, uncrossed, made from HN-38 linear polarizer sheets.

Figure 5.2: Discrete LTMA polarizers, crossed, made from HN-38 linear polarizer sheets. Note some leakage in the blue end of the spectrum.

Figure 5.2 shows a pair of discretized LTMA polarizers with their transmission axes crossed.

Polarizing Dye: Squeegee Method

Samples of two polarizing dyes, referred to as Dye #8 and Dye #27, were obtained from a company called American Polarizers Incorporated, known simply as API from here on. It was disclosed that for API's polarizers, Dye #27 worked, and Dye #8 did not work for their polarizers, due to clumping. The composition of these dyes is unknown, but they are believed to be a colloidal solution of polarizing crystals. Upon inspection of Dye #8 with an electron microscope, it was revealed that the dyes are molecular in composition. If the dye was a suspension of crystals, they should have been

seen. An image of Dye #8 obtained from the scanning electron microscope is shown in Figure 5.3.

Figure 5.3: Scanning electron microscope image of Dye #8. Each tick mark represents 20 μm .

Upon further communications with API, it was revealed that a gentleman, unnamed, experimented with these dyes some years ago to create a polarizer, with *Little Bo Peep* ammonia and glass as the substrate.

For these set of experiments the materials used include: Dye #8, Dye #27, household ammonia, an eye dropper, glass microscope slides, a straight edge and paper towels.

To ensure these dyes did work as polarizing agents, a linear polarizer was first attempted. A few drops of household ammonia were applied to a glass slide from the eye dropper and then immediately wiped off with a paper towel. Then, two drops of Dye #27 were applied at the edge of the glass slide, and using a straight edge and a paper towel the dye was smeared in a linear fashion across the slide. The dye dried fairly fast, on the

order of a second or two, and a linear polarizer was the result. It did not reach extinction, but did darken as another linear polarizer was rotated in front of it.

Knowing that a linear polarizer could be made from this dye, a LTMA polarizer was next attempted. A few drops of ammonia were smeared on slides along a semi-circular path. Once the ammonia dried, Dye #27 was applied along the bottom edge of the slides with an eye dropper to ensure the dye would coat the slides. Then, taking a paper towel over top of a straight edge, the dye was smeared onto the slides in the semi-circular fashion. Very light hand pressure was applied to the straight edge.

A linear polarizer was placed in front of the sample and rotated. What resulted was that the sample did polarize slightly and it polarized with varying transmission axes across the length of the sample. However when one of the sample slides was slid in front of the other in a linear fashion, attenuation did not occur. This was probably due to the uneven distribution of the dye across the sample.

Knowing Dye #27 did produce a multiple axis polarizer, Dye #8 was next to test. Due to the messy nature in preparing the previous sample, this sample used only one slide and the pattern was generated free-hand. The slide was secured, ammonia applied, and dye smeared just as the previous sample. Although a free hand pattern was not as precise as a traced pattern, this sample also exhibited multiple axis polarization along the length of the sample. Again however, no attenuation occurred when the previous sample was linearly slid passed this sample.

Variations of this experiment were performed using Dye #8. In one instance, the ammonia was replaced with isopropyl alcohol. No polarization resulted when isopropyl alcohol was used. In another instance, no ammonia or alcohol was used to pretreat the slide. In this instance, the surface of the glass slide was scratched with 2400 grit sandpaper in a semi-circular manner. The slide (scratches toward ink) was then floated on the ink for about two minutes. The ink only adhered to the slide where it was scratched and at first there was no polarization. But after the ink was allowed to dry, the sample

was re-examined three days later, and polarization along the path of the scratches occurred.

Once the small samples were made on the glass slides, larger polarizers were attempted on sheets of plastic. Dye #27 was tried first. The plastic sheet was scratched with 2400 grit sandpaper in the shape of the pattern. The scratched sheet was then treated with ammonia. As soon as the ammonia dried, Dye #27 was applied with a straight edge and paper towel along the path of the scratches. The process was repeated to create a second sample.

The same procedure was used with Dye #8. Two more dense polarizers were created. This is because the amount of dye that was used was greater. Again, these samples worked very well as far as having multiple transmission axes; however they did not attenuate light by sliding one past another. In addition, there were some problems with clumping of Dye #8.

Polarizing Dye: LTMA polarizer

Upon informing API of these results, two attempts were made at creating a LTMA polarizer. The first attempt, which was successful, used polarizing Dye #27 and a non-computer generated image of the pattern.

For API to create a LTMA polarizer, the pattern must first be etched on an embossing plate. The plate is aluminum, type 1100 H14 #8 with a mirror finish. Its size is 23 inches by 27.5 inches and 3/32 inches thick. The plate is shown in Figure 5.4.

This plate was then set up in a jig to etch seven, three inch semi-circular patterns side by side, as seen in Figure 5.5. The etching of the plate was done by a rubber squeegee with its blade treated with rotten stone, a polishing agent. A section of the etched patterns on the plate can be seen in Figure 5.6.

Figure 5.4: Un-etched aluminum plate from API.

Figure 5.5: Aluminum plate in jig, ready to be etched.

Figure 5.6: Section of etched aluminum plate ready for embossing.

Once the plate was made, it was taken to API to emboss sheets of cellulose tri-acetate. The etched plate was attached to a roller and heated to approximately 300 °F. Once the plate was heated, the cellulose tri-acetate was run through the roller, with the plate applying approximately 70 psi of pressure to the cellulose. To finish the polarizer, the embossed cellulose was then run through an ink bath, and then dried at about 90 °F.

The resultant product accomplished the goals of polarizing light with multiple transmission axes and it attenuated light by crossing the transmission axes with a linear translation as opposed to an angular rotation. However, total attenuation of light does not occur with this LTMA polarizer. This is believed to be due to the amount of dye used on the polarizer but it can be due to any of a multitude of different variables in the creation process. Figures 5.7 and 5.8 illustrate the resulting LTMA polarizer, first uncrossed, then crossed, respectively.

Figure 5.7: Uncrossed LTMA polarizer made from non computer generated pattern.

Figure 5.8: Crossed LTMA polarizer made from non computer generated pattern.

The second attempt used the exact same conditions as the first attempted LTMA polarizer, with one exception; the pattern used in the second attempt was computer generated. The resulting product did not exhibit any polarizing characteristics whatsoever. No attenuation occurred as the second attempt was crossed over itself, and furthermore, no attenuation occurred along different local axes. The second attempt used the same amount of polarizing dye as the first attempt. Therefore the dye cannot be the reason the second attempted polarizer failed. It is believed that there were not enough lines per inch in the computer generated pattern, which did not induce enough stress into the substrate for the polarizing ink to be effective.

Once having a working finished product, the polarizer was re-examined with the scanning electron microscope. The dye used for the LTMA polarizer was Dye #27. What was attempted here was to find crystals aligned along their long axis in grooves. What is found in Figures 5.9 – 5.12, is there are no crystals lying in the grooves of the polarizer substrate. There are no crystals at all, which means the Dye #27 is also molecular in composition. It is believed that stress from the embossing process aligns the dye molecules.

Figure 5.9: Polarizer from API at 1.00 μm. The ridges can be seen from the embossing operation.

Figure 5.10: Another view of polarizer from API. Each tick mark is 100 nm.

Figure 5.11: Attempt to find dichroic crystals lying in grooves for API polarizer.

Figure 5.12: A second view of API polarizer at 500 nm. No elongated crystals can be seen in grooves.

Iodine Polarizer: Squeegee Method

The key materials obtained for this method include: Solid iodine (I_2), Potassium iodide (KI), Boric Acid powder, Zinc Chloride ($ZnCl_2$), an unmarked bottle (concentration unknown) of liquid polyvinyl alcohol (PVA), tap water, sheets of overhead transparencies (as a substrate) and a rubber squeegee.

The first step was applying the PVA to the transparencies. The object was to induce a stress into the PVA as it dried so the resulting stress lines were in the form of the pattern in Figure 1.2. This was attempted by repeatedly passing over the liquid PVA with the squeegee until the PVA was dry. The squeegee traced along a template to give the semi-circle pattern with pressure to the PVA varying from moderately heavy pressure, by hand, to very light pressure as the PVA dried, respectively. To determine if any stress was induced into the PVA, the PVA coated substrate was placed between two crossed linear polarizers. No photoelastic effects were observed. This means one: there were no stresses induced into the PVA or two: it is possible the induced stress was not strong enough to be detected.

The next step taken was to prepare the iodine and boric acid solutions. These were prepared in accordance with Patent 4,166,871 with ± 0.5 grams precision. The iodine solution consists of iodine, potassium iodide, and water in the ratios of 1/15.82/328 by weight, respectively, and the boric acid solution consists of potassium iodide, boric acid, zinc chloride and water in the ratios of 1.95/1.25/1.0/25.67 by weight, respectively [14].

Once the solutions were prepared, the stressed PVA was dipped into the iodine solution for 15 seconds. The PVA was then removed from the dye and all excess was allowed to drip off. The stained PVA was then placed in the boric acid “fixing bath” for 25 seconds and all excess was allowed to drip off.

Instead of having a LTMA polarizer, a sheet of stained PVA was all that resulted. No polarization occurred, and it is believed the dried PVA was allowed to rehydrate or dissolve while being dipped into the solutions, thus releasing any stresses that were induced into the PVA.

To remedy this problem of releasing the stresses in the PVA, a new sheet of stressed PVA was then exposed to pure iodine. Since molecular iodine is highly reactive it was thought the iodine would bond to the long chain-like polymers of the PVA. Also, since the stressed PVA was exposed to molecular iodine, the PVA would not liquefy and no induced stresses would be released. But again no polarization occurred.

It was then decided to determine what would happen if the PVA and iodine solutions were mixed together in liquid form first. The iodine should still bond to the long polymer chains, but while the mixture is still in liquid form, it can be spread along the substrate in the desired pattern. To conduct this experiment, a few drops of the iodine solution were mixed with some liquid PVA, not in any distinct proportions, but such that the amount of PVA was much greater than the iodine solution, by volume. This mixture was then repeatedly smeared onto a plastic substrate in the form of the pattern until it dried. There again was no polarization.

It was only when the boric acid solution was mixed with the liquid PVA and iodine solution that polarization occurred. As in the previous attempt, a few drops of the iodine solution were mixed with some liquid PVA in non-distinct proportions. In this attempt however, a few drops (about the same amount by volume of the iodine solution) of the boric acid solution were also mixed in with the liquid PVA and iodine solution. The mixture turned dark violet in color and some slight precipitation occurred. The precipitate seemed to have a coagulated gelatin like texture, very thick and very stretchy. This mixture was then repeatedly smeared onto a plastic substrate with a squeegee in a semi-circular manner as was done in every previous attempt until the mixture had dried. Although most of the prepared sample showed no signs of polarization, certain small areas, mostly in the areas of the precipitate, did polarize light. Each polarizing area had a different transmission axis depending upon where in the pattern it was found!

Although most of these attempts were disappointments, they were all kept for later study. However, after a few days, it was noticed that the samples that were dipped into the solutions began to crystallize and lose their color! This is for reasons unknown, although it is believed that the samples dehydrated and one or more of the compounds (boric acid, zinc chloride, potassium iodide) crystallized.

Chapter 6: Conclusions and Recommendations

The idea of having a polarizer attenuate light by translation as opposed to rotation is viable. This is realized in the discretized LTMA polarizer. Although a continuous sheet is desirable, the discrete LTMA polarizer proves the concept works.

When using Dye #27, polarization often occurred in the direction in which the dye was applied to the sample. It is believed that while the dye is still in liquid form, shear stress induced into the dye, allowed the molecules to become aligned. If the dye dried soon after application, the orientation of the molecules along the shear stress was preserved, otherwise the molecules become disoriented. Furthermore, the strength of the polarization is also dependent upon the amount of dye on the polarizer. It is also believed that polarizing Dye #27 is a molecular solution and not a colloidal solution of crystals or any other suspended substance.

In creating the LTMA polarizer with API, pressure was important in the fabrication process. The pressure from the embossing plate allowed ridges to be created in the polarizer substrate. It's believed these ridges induced stress into the substrate which allowed the dye molecules to align in a preferred direction. If the induced stress on the polarizer is not great enough, the polarization effects will be poor. This was seen in a failed attempt from API using a computer generated pattern.

Stress was also important in the attempts to create the polyvinyl alcohol based iodine polarizer. Because the iodine solution removed any stress induced into the PVA, there was no resulting polarization. However, when the iodine solution and PVA were mixed in liquid form, along with the boric acid solution and that mixture was applied, polarization occurred when parts of the mixture that coagulated were stressed by the squeegee along the pattern. It is also believed in the unsuccessful samples, if the iodine impregnated PVA was heated to make it more pliable, and then stressed by the squeegee, a LTMA polarizer would have also resulted.

It is recommended the attempts at the PVA and iodine type of polarizer be attempted once more; this time, the temperatures of the iodine solution and the boric acid solution should be at their respective elevated temperatures as in Patent 4,166,871. If that attempt fails, stressing the PVA after the iodine and acid solutions have been applied should be tried, perhaps by an embossing operation. In addition, if an embossing operation is feasible, a sheet of birefringent material such as Tenite should also be embossed. The embossing should produce a LTMA polarizer in the Tenite as well, and no polarizing ink should be necessary.

One other recommendation would be to obtain some viscous solution, almost paste-like in nature that has a high evaporation rate, and suspend silver or aluminum particles (about 100 nm long by 10's of nm wide) in it. This metallic paste would then be applied to a suitable substrate by a squeegee along a semi-circular path. The squeegee would create a shear stress in the paste, and should align the metal particles along the path. The outcome would be a semi-reflective, semi-transmissive multi-axis polarized mirror.

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