Process Modifications for Improved Optical Characteristics of K-Type Polarizer

by

Stephanie K. Dalquist

S.B., Chemical Engineering
Massachusetts Institute of Technology, 2003

Submitted to the Department of Materials Science and Engineering
In Partial Fulfillment of the Requirements for the Degree of

Master of Engineering in Materials Science and Engineering

at the

Massachusetts Institute of Technology

June 2003

© 2003 Stephanie K. Dalquist
All rights reserved

The author hereby grants to MIT permission to reproduce and to distribute publicly paper and electronic copies of this thesis document in whole or in part.

Signature of Author:

Department of Materials Science and Engineering
May 9, 2003

Certified by:

Michael F. Rubner
TDK Professor of Materials Science and Engineering
Thesis Supervisor

Accepted by:

Harry L. Tuller
Professor of Ceramics and Electronic Materials
Chair, Departmental Committee on Graduate Students
Process Modifications for Improved Optical Characteristics of K-Type Polarizer

by

Stephanie K. Dalquist

Submitted to the Department of Materials Science and Engineering on May 9, 2003 in Partial Fulfillment of the Requirements for the Degree of Master of Engineering in Materials Science and Engineering

ABSTRACT

Synthetic sheet polarizers have a wide range of purposes, primarily in liquid crystal displays (LCD), in particular those with anti-glare and contrast-enhancing applications. Current polarizers do not perform to their full potential due to "leakage" in the red and blue parts of the spectrum, where light in the axis of polarization is inefficiently transmitted at wavelengths along the edge of the visible light spectrum. The absorption peaks can be spread to absorb light at the outer visible wavelengths by adding dichroic dyes to correct the blue (400-450 nm range) or red leakage (620-660 nm).

This project covers experimentation to determine the value of these process additions and to further the understanding of the new mechanisms and the improvements they bring. This new polarizer is still in the technology development phase, but could be commercialized with these advances, giving 3M a competitive advantage in the current polarizer industry and in new applications which demand high durability and truer blacks.

Thesis Supervisor: Michael F. Rubner
Title: TDK Professor of Polymer Materials Science and Engineering
Director, Center for Materials Science and Engineering
Acknowledgments

This thesis would not have been possible without the support of several people who were interested in the work and believed it could be done.

Everyone at 3M Optical Systems Division in Norwood, Massachusetts, has been of great help in teaching me the science and techniques behind K-polarizer, as well as its history and future. In particular, Jon Mack and Pradnya Nagarkar have put a lot of time into introducing me to polarizer manufacturing and the intricacies of working with new technology in industry. Ann Tennis taught me a lot about the division's past and near future while sparing me from the bitter New England winters, and Giorgio Trapani provided me with specifications on competitor products and assistance in explaining the science of polarization for professors, managers, and everyone in the middle.

The M.Eng. program would not have been so successful without the hard work of the program director, Professor Eugene Fitzgerald, Professor Michael Rubner, who has generously given time to be my thesis reader, and the staff in graduate programs for Materials Science here at MIT.
Biographical Note

Stephanie K. Dalquist was born on September 20, 1981, near Minneapolis, Minnesota. Always interested in sciences, she began attending the Massachusetts Institute of Technology in 1998, graduating with a S.B. in Chemical Engineering in 2002. She first became involved with the K-polarizer project in the summer of 2001, when she interned with 3M and was selected as a 3M scholar. Returning to the Optical Systems Division seemed the perfect opportunity in a Master’s program with a focus on emerging technologies.

She was also a member of Ælo Pròp, which won the developmental entrepreneurship division of the 2001 MIT $1K Entrepreneurship competition, co-author of the paper “Origins of Anomalous Micellization in Diblock Copolymer Solutions,” published in Langmuir, and an academic essay on the cultural analysis of science fiction in Performing the Force, edited by Kurt Lancaster and Thomas Mikotowicz. Besides polarizers, Stephanie’s engineering interests lie in sustainability, in which she has worked on projects with the United Nations Environment Programme and the École Polytechnique Fédérale de Lausanne. While at MIT, she has also had the opportunity to teach chemistry, French, and English as a second language. Her other interests include reading, travel, cooking, and learning foreign languages (Spanish, French, German, Russian, and Mandarin). Next year she will begin in the sustainability track of the MIT Technology and Policy Program.
Table of Contents

Abstract ................................................................................................................. 3
Acknowledgements ............................................................................................... 4
Biographical Note ................................................................................................. 5
Table of Contents ................................................................................................. 6
Table of Figures .................................................................................................... 7
Table of Tables ..................................................................................................... 7
1.0 Introduction ..................................................................................................... 8
  1.1 How Polarizers Work ..................................................................................... 8
  1.2 Why Polarizers are Necessary in LCDs ....................................................... 10
  1.3 What is Available Today .............................................................................. 13
  1.4 K-Polarizer History ...................................................................................... 16
2.0 Process ............................................................................................................ 17
  2.1 Materials and Methods ............................................................................... 18
  2.2 Previous Developments .............................................................................. 20
3.0 Objectives ...................................................................................................... 20
  3.1 Approaches ................................................................................................. 24
  3.2 Results ......................................................................................................... 24
    3.2.1 Analysis ................................................................................................. 24
    3.2.2 Blue Dye ............................................................................................... 25
    3.2.3 Yellow Dye ............................................................................................ 27
4.0 K-Polarizer Applications ............................................................................... 28
  4.1 Automotive Applications ............................................................................ 30
  4.2 High-end LCD Displays ............................................................................ 33
  4.3 Other Industries ........................................................................................... 35
  4.4 Challenges .................................................................................................. 36
5.0 Intellectual Property ....................................................................................... 37
  5.1 Concentration of Current Intellectual Property ....................................... 37
  5.2 Blocking Intellectual Property .................................................................... 39
  5.3 Patent or Trade Secret? ................................................................................ 39
6.0 Conclusions ................................................................................................... 41
Appendix A. Relevant Patents ............................................................................ 42
References ........................................................................................................... 46
Recommended Reading ....................................................................................... 48
Table of Figures

Figure 1. Unpolarized light travels in all directions ................................................................. 9
Figure 2. Unpolarized light can be polarized by sending it through a polarizer film ................................................................. 9
Figure 3. Visual diagram of a liquid crystal display ...................................................................... 12
Figure 4. A German intelligent credit card ................................................................................ 14
Figure 5. The world production of polarizers is centered around the manufacturers of LCD displays ................................................................................................................ 15
Figure 6. Reaction scheme for the preparation of poly(vinylalcohol-b-acetylene) ... 18
Figure 7. Absorbance of control and blue-dyed K-polarizer .......................................................... 26
Figure 8. Absorbance of control and yellow-dyed K-polarizer ...................................................... 26
Figure 9. Number of 5.5 to 8 inch LCD displays sold for automotive applications, by year ................................................................................. 31
Figure 10. Automotive LCD applications like GPS navigation must withstand extreme environments, for which K-polarizer is ideally suited ..................................................................... 32
Figure 11. Sales of flat panel displays worldwide, in billions of dollars .................................... 34

Table of Tables

Table 1. Key Design Criteria for K-Polarizer ................................................................................ 21
1.0 Introduction

Since their invention in 1928, sheet polarizers have played an important role in the development of display technology. Inspired by the light-changing qualities of minerals like quartz, Edwin Land invented the sheet polarizer to be used in automobile headlights to reduce glare. In the last seventy years, sheet polarizers have become an integral part of technologies from infrared goggles to laptop displays, and have spawned new varieties over the years in an international race to the best optics and durability. The process improvements explored through this project may finally bring together the finest characteristics to outperform top of the line iodine polarizers, the industry standard, in terms of color neutrality, efficiency at given average transmission ($k_a$) and environmental stability.

1.1 How Polarizers Work

Ordinary light is unpolarized, consisting of rays vibrating equally in all directions in a plane perpendicular to the direction of propagation. The unpolarized state is typically represented in vector geometry as two equal components vibrating orthogonally to one another (see Figure 1).
Figure 1. Unpolarized light travels in all directions. Plane polarized light only travels along the polarizer's axis of transmission.

In a sheet polarizer, the transmission axis is the direction in which polarized light is transmitted (see Figure 2). When light is intercepted by a polarizer, all light which is not traveling parallel to the axis of transmission is blocked. For many applications, like glare reduction, only one layer of polarizer is needed. As an example, a layer of polarizer on sunglasses will reduce glare from headlights or snow by blocking all light which is not parallel to the axis of transmission.

Figure 2. Unpolarized light can be polarized by sending it through a polarizer film. A second polarizer can block the polarized light or let it pass, depending on the axis of transmission.
The most interesting applications arise when a second polarizer is layered over the first\textsuperscript{3}. In this case, as expected, any light that passes through the first polarizer is in line with the axis of transmission of the first polarizer. The second polarizer, however, may be parallel to or crossed with the first. In the case that the polarizers are parallel, the axes of transmission are aligned, and light that passed through the first polarizer will also pass through the second, and a viewer on the far side of the polarizers will see light. If the polarizers are crossed, however, the light that passed through the first polarizer and is aligned with its axis of transmission will be perpendicular to the second polarizer and its axis of transmission, and a viewer will not see any light transmitted. Furthermore, the ideal polarizer will be of a neutral grey when uncrossed, and near black when crossed. Current iodine polarizers have a dark green tinge, as evidenced in any laptop display, but when crossed are so close to extinction as to appear color neutral\textsuperscript{4-6}. This peculiar property is the basis of modern display technologies.

1.2 Why Polarizers are Necessary in LCDs
By far the biggest market for sheet polarizers, and K-polarizer in specific, is the flat-panel display industry. Around $30 billion of flat-panel displays were sold in 2003, and revenue is expected to grow around $20 billion per annum until 2010\textsuperscript{7,8}. Laptops and personal digital assistants (PDAs) becoming commonplace, flat-panel displays are now commonly sold with new desktops and being purchased as stand-alone units to replace aging CRTs with a much larger footprint. Displays are also being added to other
appliances and devices to increase functionality, provide information to users, and reduce the number of breakable parts. Every flat-panel display, mostly LCDs at this point, requires at least one and usually two layers of sheet polarizer, ensuring that polarizer manufacturers will be in business for years to come.

Liquid Crystal Displays were first invented by Schadt and Helfrich and demonstrated by Fergason in 1971\(^2\), who sandwiched liquid crystal between two polarizers and controlled the birefringence electrically. Flat-panels work much the same today, as column and row drivers control the voltage applied at each pixel's electrode.

The most common LCD, called a twisted nematic, uses the same light-blocking property that makes a single layer polarizer useful in reducing glare from environmental surroundings. Liquid crystal (LC), an inorganic polymer, is brushed on the surface of transparent electrodes. The cigar-shaped molecules tend to orient their long axes along the direction of application. The glass-plated electrodes, coated in polymer, are now sandwiched so that the rub directions and the long dimension of the LC molecules are perpendicular to each other. Sheet polarizers are affixed to the outside of each glass electrode, with the transmission axis matching the rub direction of its adjacent glass plate\(^9\). Because the LC on each electrode is oriented along a different direction, the polymer, when sandwiched together, aligns to undergo a smooth twist within the cell, acting as an optical wave guide. Unpolarized light first enters a polarizer (Figure 3), where only light traveling parallel to the axis of transmission is passed to the LC
molecules. The smooth twist of the LC molecules acts as a wave guide, rotating the plane of polarized light by a

![Diagram of liquid crystal display](image)

**(A) Unpolarized Light**

Unpolarized Light

Electrodes

E=0

Analyzer

Polarized Light

**(B) Unpolarized Light**

Unpolarized Light

Electrodes (Voltage on)

No Light

**Figure 3. Visual diagram of a liquid crystal display.**

quarter turn. Upon reaching the second polarizer, the light can pass through it, and the LC is transparent.

Liquid crystal molecules, like other polarized molecules, will align themselves along an electric field (E, in Figure 3) when one is present. This alignment disrupts the smooth twist of the LC between electrodes, and thus the LC does not guide the polarized light through the second polarizer, and the cell is dark, since all light is blocked at the second
polarizer. When the electric field is removed, the molecules relax and return to their original state\(^9\).

The application of electric fields to each pixel determines the output of displays, and the sheet polarizers are necessary for the display to work. As in all technology, the ideal polarizer does not actually exist, and thus polarizers are usually categorized by their efficiency at a given \(k_0\), color on the CIELAB scale, and according to other customer specifications, such as environmental durability, scratch resistance, and glare reduction properties. Such a variety ensures that whatever the requirements of the display product, there is a polarizer to match.

1.3 What is Available Today

Many different flavors of sheet polarizer are available today, and customer specifications can be met by any of the major manufacturers to serve different applications. Most applications are served by one of two major technologies, and both types of polarizer are available from several major companies and a few smaller ones.

Iodine polarizers are the industry standard, and were first developed in 1928. Since then, their optics have improved greatly, and polarizers can now be made for devices that require good color (e.g., laptops, televisions, and other flat-panel displays) or high efficiency (e.g., laptops, mobile phones, personal digital assistants, also known as PDAs). Middle and lower quality iodine polarizers are still frequently made for cheap and disposable applications\(^10\), like the intelligent credit card (Figure 4). The iodine polarizer
begins as polyvinyl alcohol (PVA) polymer film, in rolls up to hundreds of meters in length. The polarization properties are an effect of the formation of a chromophore, or chemical complex, between the PVA and the tri-iodide ion it is exposed to under heat\textsuperscript{12}. The quasi-stable chromophore complex has limited the application of iodine polarizers in automotive, avionics, and projection system applications where the final product must operate over broad environmental extremes\textsuperscript{13}.

Dyestuff is more suited for such applications, which has horrible optics but outstanding durability. Where iodine polarizers will bleach in a hot, humid environment (80°C, 80% relative humidity) within 10 hours, the optical quality of dyestuff will not degrade for a couple thousand hours\textsuperscript{3-5}. Though it does not degrade easily, the optical quality is inferior to other polarizers. Dyestuff is made by coating polyvinyl alcohol thin film with dichroic dye in solution and then stretching it to align the dye molecules. In general, dichroic dyes are cigar-shaped molecules\textsuperscript{14}. When viewed head-on, their cross-section is
small and thus not visible to light, but when rotated they becomes highly visible, providing polarization to an otherwise optically inactive material. Because each dichroic dye is optically active in only one narrow range of wavelengths, it is necessary to incorporate several dichroic dyes into one film to view full-color displays. The combination of dyes means that every wavelength can be viewed, but they are all blocked at different wavelengths by the other dyes, and the end result is a murky, inefficient polarizer.

Both types of polarizers are made by several companies around the world, most of them in Japan. Over half of the polarizers in the marketplace are made by Nitto Denko Corporation of Osaka, Japan. Other major competitors include Pola-Techno, Sumitomo Chemical, and Sanritz of Sanritsu Electrical Co., Ltd., all of Japan. There are a few small

![Pie chart](image)

**Figure 5.** The world production of polarizers is centered around the manufacturers of LCD displays. Most of these companies are in Asia, as shown above. Market share determined by quantity sold.
start-ups in China and Taiwan, and few polarizer manufacturers outside of Asia (Figure 5). With billions of dollars of sales worldwide and a growing number of applications, iodine and dyestuff polarizers will continue to be a major part of the future, and K-polarizer could soon join them.

1.4 K-Polarizer History (1926-2000)

The KE2 polarizer is still nascent technology, but carries a colorful seventy year history and connections to some of the most innovative players in scientific research. In 1926, a young Harvard dropout set a goal for himself – Edwin Land wanted to develop polarizers for automobile headlights, reducing the glare seen by drivers in the increasingly popular automobile\(^\text{15}\). By 1928, Land-Wheelright Laboratories had developed the first plastic sheet polarizer, with which he received his first patent in 1933. The government and automobile industry did not warm to his product, though, and the polarizers went into diverse applications including sunglasses and desk lamps\(^\text{16}\).

Despite this early setback, Land set his sights on the automotive industry, and kept this research alive as the Polaroid Corporation (established 1937), named for his glare-reducing polarizer, grew into a manufacturer of consumer and military products\(^\text{17}\). One of the greatest drawbacks to Land’s early polarizers was their inability to withstand conditions of extreme heat and humidity frequently encountered by automobile components\(^\text{15}\).
To withstand these conditions, Land and his colleague Howard Rogers abandoned the iodine-based structures and invented K polarizer in 1939. K sheet started as a thin film of polyvinyl alcohol (PVA), which could be stretched at high ratios to orient the long chained molecules, then converted to polyvinylene through selective dehydration. The carbon-carbon double bonds formed gave “intense directional light absorption”\textsuperscript{15}. Despite tentative agreements during World War II, during which civilian car manufacturing was at a standstill, General Motors and the Automotive Manufacturers Association dropped plans to include glare-reducing polarizers in headlights\textsuperscript{15}.

K sheet continued to be manufactured for high-durability applications, and the manufacturing plant moved to land leased from a Cambridge engineering school known as MIT. Polaroid made K polarizer at the current site of the MIT Media Lab until the early 1980’s, when the lease was cancelled to make room for the Wiesner Media Arts Laboratory. The Polaroid Park development in Norwood, Massachusetts, became the new plant site. Due to increasing financial difficulties and lost business opportunities, Polaroid was forced to put the polarizer division up for sale in 1999. On April 3, 2000, the division was purchased by the Minnesota-based Minnesota Mining and Manufacturing, better known as 3M\textsuperscript{18}.

2.0 Process

Since its invention in 1939, the manufacturing process of K-type polarizer has been scaled up and improved to reach the optical and durability standards of the current material. K-polarizer starts as rolls of thin film polyvinyl alcohol (PVA), just like iodine
and dyestuff polarizers. However, instead of forming unstable complexes or coating the film with oriented molecules, K-polarizer is made by the thermal dehydration of oriented PVA films with an acid catalyst\textsuperscript{13} (Figure 6). The reaction generates carbon-carbon double bonds, or \(-\text{(-C=C-)}_n\) conjugation along the polymer backbone, incorporating the chromophore directly into the chemical structure. The resulting product is a block copolymer of vinylalcohol and acetylene (PVA/PAC)\textsuperscript{13}.

![Chemical structure diagram]

**Figure 6.** Reaction scheme for the preparation of poly(vinylalcohol-b-acetylene)\textsuperscript{13}.

2.1 Materials and Methods

Much like iodine and dyestuff polarizers, K-polarizer is prepared from a film of PVA, starting at a thickness of around 3 μm. The film is heated to around 150°F, then stretched at an even higher temperature, around 250°F, to several times its original length. At the
time the last paper was publicly presented on K-polarizer in 1997, the maximum stretch ratio\textsuperscript{13} was only $L/L_0 = 3.6$, where $L$ represents the final length and $L_0$ the original length of the roll. Current processes are routinely run at 6.0 or 6.5 stretch ratio, and can achieve much higher efficiency at a given $k_r$ as a result of these advances. Over the years, PVA manufacturers have made available films of a higher degree of polymerization ($D_p$) which have also contributed to the improved optics of K-polarizer. There is a limit to the effectiveness of both of these factors; at some point both increased stretch ratio and increased $D_p$ will not additionally contribute to the polarizer optics. Investigating new methods, like the incorporation of dichroic dyes, now means new routes for improvement are being explored before the current paths come to a dead end.

The stretched PVA is then exposed to an acid catalyst in vapor phase (Figure 6). The PVA film is suspended in the headspace above a solution of acid, with a residence time around 90 seconds. The acid is kept at a temperature between 35°C and 60°C, and will be absorbed anywhere within that range\textsuperscript{13}. Dehydration can only be controlled by keeping it at a constant temperature, however. The acid-coated PVA film proceeds into an oven (160°C, 2 minute residence time) to affect the dehydration reaction\textsuperscript{13}. Upon emerging from the oven, the PVA has been converted from a transparent film to a distinctive reddish brown.

Exploration in improving the manufacturing process is currently focused in the third and final step of manufacture, where the polarizer undergoes a second stretch. Any support materials are removed, and the film is stretched an additional 10% to 60% for a final
extension ratio $L/Lo \approx 6.5-7.0$. The restretch is performed in an aqueous solution of boric acid and borax (9% and 3% wt/volume) at a temperature of 70°C. Much of the required residence time (5-10 minutes) is required for the material to swell and neck in perpendicular to the stretch direction. A final bath is used to wash the polarizer with distilled water to remove chemicals and prevent further reaction. This step is notable for improving K-polarizer efficiency and converting the material from the reddish-brown of the intermediate step to the neutral grey desired for display applications.

2.2 Previous Developments

The process described here includes several recent proprietary developments which have been incorporated to improve optics and improve consistency crossweb and downweb. The process speed can be controlled to achieve a consistent stretch ratio, permitting a high degree of molecular orientation as needed for high efficiency product. Another development controls the dehydration kinetics in the presence of the vapor acid phase. Optical quality can be measured and adjusted in real time to control the distribution of conjugation lengths of polyacetylene segments within the PVA. Conjugation length is one of the prime factors which determine the wavelength range in which the chromophore absorbs light. For the final optical push that K-polarizer needs to compete with top of the line iodine polarizer, new process improvements must be still considered.

3.0 Objectives

K-polarizer has come a long way since its invention, but is still in a phase of technology development, from which it must mature before commercialization can occur. The
technical objectives treated in this project are key to the eventual market release of K-polarizer.

Although K-polarizer already delivers incredible environmental stability and good optics, there is room for improvement before the material is released to display manufacturing clients. By surpassing these obstacles, K-polarizer will prove formidable competition to the conventional iodine and dyestuff polarizers in their respective markets.

It has been shown\textsuperscript{12} that details of polarizer processing determine properties of the assembled display (Table 1). Every one of these goals achieved raises the bar of final display quality, but their importance must be prioritized according to the capabilities of K-polarizer and the requirements of the intended customer.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Property</th>
<th>Controlling Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optics</td>
<td>Polarization Efficiency</td>
<td>Molecular orientation</td>
</tr>
<tr>
<td></td>
<td>Color Rendition</td>
<td>Kinetics of chromophore formation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chromophore distribution</td>
</tr>
<tr>
<td>Durability</td>
<td>Polarization</td>
<td>Chromophore type</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(e.g. Iodine, vinylene, dyestuff)</td>
</tr>
<tr>
<td></td>
<td>Adhesion</td>
<td>Chemistry</td>
</tr>
</tbody>
</table>

Table 1. Key Design Criteria for K-polarizer\textsuperscript{12}. 
Design factors like those above guide the objectives for future K-polarizer development. The strongest trait of K-polarizer is its durability, where carbon-carbon double bonds in the polyvinylene backbone maintain the polarization and adhesion qualities despite environmental extremes, making it one of the most stable chromophores available. Optically, it is also a good product, but does not yet meet the rigorous objectives required by 3M and its clients. To reach release goals and be competitive with top of the line iodine polarizer products, the highest priorities are to

- Increase polarization efficiency\(^5\) – competing high durability iodine polarizers can reach a polarizing efficiency of 99.95%, but at a \(k_v\) of about 36
- Reach color neutrality\(^5\) – competing super high contrast iodine polarizers can attain a crossed b* of 0 at 99.975% efficiency and 44.3 \(k_v\).

Both of these characteristics have significant impact on the quality of the final display, and reaching these objectives in polarizer quality will improve the optical qualities of any display they are used in.

Polarization efficiency is defined by

\[
\eta = \frac{k_1 - k_2}{k_1 + k_2} \tag{1}
\]

where \(k_1\) is transmission in the pass-through state and \(k_2\) is transmission in the crossed state. The higher the efficiency of the polarizer, the greater the difference between \(k_1\) and \(k_2\). Because polarizers block any light not in line with the axis of polarization, the effect can be described as the result of having a polarizer with less orientation of the polymer chains, resulting in a lower \(k_1\), higher \(k_2\), and thus lower efficiency. For this reason,
attempts to reach higher efficiency has focused on increased stretch ratio\textsuperscript{12}, which forces the polymer chains to align themselves along the axis of transmission. Top of the line iodine polarizers have efficiency around 99.9\%, and to succeed, K-polarizer should be at least this good. High efficiency polarizers are particularly important for LCDs on high content and portable displays. Among other things, high efficiency lowers power requirements for a given brightness. Since the polymer chains are more highly oriented, the axis of transmission is better defined, and less light is blocked within it. This means that a laptop display could require the same amount of power and have a brighter display than today’s standard, or that at the same brightness level the battery could store the same energy but allow more time between recharges\textsuperscript{19}.

Improving the color of the polarizer is more complex, as there are three axes along which color is determined. Display color is frequently measured using the CIELAB 1972 standard. The three axes of measurement are L (luminance, which ranges from 0 (black) to 1 (white)), a* (which measures $-a^*$ (green) to $+a^*$ (red)) and b* (which measures $-b^*$ (blue) to $+b^*$ (yellow)). The ultimate goal is to achieve a polarizer of neutral color with crossed a* and b* of 0. Standard polarizers today have a wide range of colors, but iodine polarizers consistently have a green tinge ($-a^*$), which is still present in final products\textsuperscript{20}. A neutral polarizer will therefore allow truer blacks and whites, making the colors more consistent, more vibrant, and easier to reproduce in print. By attaining these goals, 3M will produce a material that can match or beat high-end polarizers in durability and optics.
3.1 Approaches

To meet the technical goals above and bring K-polarizer to the optical quality needed for commercialization, several methods are being researched at the final stages of manufacture, where the chemical reactions take place within the PVA. There are several approaches being considered at this time, but at this time most cannot be discussed in detail for reasons of confidentiality. One of the most promising new processes investigates changes in the final step, the boration of K-polarizer.

After the dehydration reaction has occurred over the vapor-phase acid, the polarizer film passes through two tanks of boric acid and borax$^{13}$. When a dichroic dye such as those used in dyestuff$^{4-6,14}$ is included in the tank solution in quantities on the order of magnitude of parts per million, the dye is absorbed into the web, producing a color in the dyed web which is noticeably different from the color of the undyed web.

The dyes are used only to correct for color, and therefore change the absorption spectrum of the polarizer. Since the polarizer has leaks in both the red and blue wavelengths at 620-660 nm and 400-450 nm, respectively, both a blue and a yellow dye were tried in the borax solution.

3.2 Results

3.2.1 Analysis

UV/Vis spectra of polarized light were recorded on a Cary 5E spectrophotometer using a Glan-Thompson analyzer. Absorbance spectra obtained with the incident plane of light
parallel to the stretch direction of the sample are denoted as $A_z$, while those obtained with the plane of polarization parallel to the transverse direction of the polarizer are denoted as $A_y$. The combined set of these analyses are denoted as $A_z-A_y$. All spectra were corrected for surface reflections.

3.2.2 Blue Dye

It was hoped that the blue dye would either spread or steepen the current peak, which begins around 700 nm and peaks at around 555 nm, or create a second peak adjacent to it, fixing the red leak in the higher end of the visible spectrum.

In the end, the blue dye did not do much at all to improve the color of the polarizer (Figure 8). Although the peak has spread a little, it is not enough to change the CIELAB color values significantly and therefore not worth the cost of the material and labor to keep it, and the polarizer, at a
Figure 7. Absorbance of control and blue-dyed K-polarizer. Note the low absorbance at both ends of the visible light spectrum.

Figure 8. Absorbance of control and yellow-dyed K-polarizer. The blue leak has been fixed with a new absorbance peak from the yellow dye.
consistent color value. Because of the lackluster results, the blue dye was only tried on the pilot machine, and not scaled up to a full-width roll.

### 3.2.3 Yellow Dye

The yellow dye, similarly, was tried with the intent to spread the primary peak or create a second adjacent peak to fix the blue leak in the lower visible wavelengths. As described above, the polarizer coming out of the borax solution had a more neutral grey color than previous runs of undyed web running at the same conditions. In bench top, pilot process, and production-sized batches, the color neutrality of the polarizer was improved by including the yellow dichroic dye.

The significance of the improvement is clear from the absorption spectrum in the visible light wavelengths (Figure 9), where a second peak is present in the Az spectrum from about 476 nm to the end of the measured spectrum at 350 nm on the outside of the visible wavelengths. Furthermore, the addition of the yellow dye to the manufacturing process did not affect the absorbance in the parallel, or Ay, state, so very little yellow color will be visible in a display when the light and top polarizer are uncrossed. In terms of CIELAB values, the undyed and yellow polarizers can be quantitatively compared. The color values, particularly crossed b*, are much closer to target values for neutrality, and the improvement has been made without compromising the k, and efficiency of the K-polarizer product (not disclosed). All color values are brought closer to neutrality, but
the $b^*$ values, which are most important at this stage, are reduced to within 10% of neutrality on the CIELAB color scale.

Although there are still other processes being explored, at least one, the incorporation of yellow dye, meets the requirements for future development with the ultimate goal of commercializing K-polarizer.

4.0 K-Polarizer Applications

Polarizers are used in a wide variety of products that require polarized light. They are manufactured to different specifications for commonplace and specialized products, consumer and military users, and anything in between. Since Land and Rogers invented the first polarizers in 1929\textsuperscript{15}, they have been used in desk lamps, aviation goggles, sunglasses, gun sights\textsuperscript{16}, and more recently, liquid crystal displays for watches, bank cards (Figure 4), laptops, and televisions, though never in automobile headlights, the elusive market that drove Land to invent sheet polarizers and pursue the high durability K-sheet polarizer for many years.

Because there are so many possible markets for polarizers, 3M has focused its efforts on the markets with the best opportunities for K-polarizer. 3M is in a unique position, in that they are aiming to commercialize a product which is, without exaggeration, made by no one else in the world.
In determining target applications, the traits of the new product can be used to focus commercialization on markets that will see improvements from its introduction. For the improved K-polarizer, the attributes which set it apart from its competition are its optical qualities and durability.

Optically, K-polarizer made with the advanced processes for polarizer explored here possesses desirable traits for many markets, including

- High efficiency
- Near color neutrality

Along with superior optical qualities, the polarizer product is among the most durable polarizers available, making it a good choice for applications which must withstand

- High humidity
- Extreme temperatures
- Precipitation.

As a business decision, K-polarizer is a sound choice because it comes with the knowledge and support of a company with established products that can provide an added value structure to the polarizer. Any polarizer by itself is of limited value – the wide range of applications and markets have developed only by combining polarizers with other components to meet the needs of the end user. 3M, which has developed and commercialized other structures used in optical systems, can meet diverse customer requirements by attaching the polarizer to other thin films, improving, for example
• Scratch resistance
• Viewing angle
• Anti-reflective qualities
• Contrast ratio

and other characteristics that will make the K-polarizer a sure choice for a certain technology.

Based on the superior optical qualities and the K-polarizer ability to withstand extreme environments, 3M has focused its commercialization efforts on two growing display industries: automotive and high-end LCD applications. Should K-polarizer become a prominent part of these markets, 3M will have the opportunity to expand the product into other niche markets with the same technology.

4.1 Automotive Applications

After a seventy year detour, Land’s dream of putting his polarizer in every car may come true. Instead of being used in automobile headlights, though, sheet polarizers will be used in displays inside the car. Already, entertainment displays, for television and video games, and informational displays, like HUDs (heads-up displays) and GPS (global positioning system) navigational systems are optional in new cars. The worldwide market for in-car displays is growing quickly. In 2002, approximately 6 million LCD displays between 5.5 and 8 inches were sold for in-car use, and the market is estimated to grow 15% over the next decade. Industry analysts predict that by 2005, new cars will contain on average six to seven polarized displays¹⁹.
Figure 9. Number of 5.5 to 8 inch LCD displays sold for automotive applications, by year\textsuperscript{19}.

K-polarizer is an apt choice for the automotive industry to use inside the car, much as it would have been the perfect polarizer for headlights, because it is a highly durable material. By creating a chromophore through desaturation of polyvinyl alcohol, the chromophore has been built into the polarizer in a stable configuration that does not rely on complexing, as iodine H-polarizers do\textsuperscript{13}. Environmental testing has shown negligible degradation of K-polarizer at 80\(^\circ\) and 80\% relative humidity over a period of 700 hours\textsuperscript{21}. Even under seemingly pleasant outdoor temperatures, like a 90\(\,^\circ\)F summer day, the inside of a car can reach 140\(\,^\circ\)F within 40 minutes\textsuperscript{22}. This sort of environment is devastating to iodine polarizers, in particular, which are susceptible to bleaching and cracking\textsuperscript{23}. Iodine-polarized displays in automobiles could be degraded from a short summer shopping trip, and completely bleached during a day at work. Compared to the longevity
of K-polarizer under extreme conditions, iodine polarizers can only be described as ephemeral, and are optically compromised after about 20 hours in the same conditions.\textsuperscript{5}

The added benefits of a wide viewing angle and increased glare reduction are important inside an automobile for both entertainment and information displays. Although automotive applications will not require the enhanced colors made possible by K-polarizer, more vibrant displays for automotive entertainment applications will be an improvement over what is currently available.

![Image](image.png)

**Figure 10.** Automotive LCD applications like GPS navigation must withstand extreme environments, for which K-polarizer is ideally suited.

The most formidable competition for the growing automotive display market is dyestuff, which is used in today’s in-car displays. Instead of being a true polarizer, where polarization property is an effect of a chromophore somehow complexed or bonded to the backbone, dyestuff is made from dichroic dyes coated and oriented along a carrier web, usually polyvinyl alcohol. Its polarization abilities derive solely from the shape and orientation of the dye molecules and PVA, rather than from a chromophoric active group. Although the optics of dyestuff are far inferior to both K- and H-polarizers, dyestuff is even more stable than K-polarizer. Under 80°C and 80% relative humidity conditions,
dyestuff undergoes minimal change in efficiency and transmission until about 1000 hours into testing. Since dyestuff is also less expensive than the sheet polarizers, 3M must focus on other strengths of K-polarizer to gain a foothold in the automotive display market.

4.2 High-end LCD Displays

The largest market for LCDs is for computers, both laptop and desktop, and the growing market in LCD televisions. In 2002, flat panels were already a strong market, bringing in approximately $30 billion dollars worldwide. Due to advances in display quality, increased popularity of laptops and LCD televisions, and business partnerships that package flat panel displays with new off-the-shelf desktops, demand continues to grow at 20% annually, and revenue is expected to top $100 billion dollars by the year 2010.

Despite the market size, rapid growth indicates that there is opportunity to introduce a new polarizer to display manufacturers, provided it can outperform the iodine standard in cost and performance. If the manufacturing process for K-polarizer can be integrated, efficient manufacturing and the savings from triacetate coating (which protects iodine from the effects of the elements in display products) will bring the costs of producing K below that of iodine, making the improved product a strong contender for
entry into a tight market based on technical and financial specifications. The environmental stability of K-polarizer is not necessary for television and computer displays, and will not be a strong selling point for the flat panel display industry. What makes K-polarizer valuable for these applications is the improved optics resulting from the new methods discussed here. Improvements which make K-polarizer viable for high-end displays include

- Near color neutrality, which results in truer blacks and whites in a final display. Iodine polarizers leave a green tint in even the best of today's displays, which can be easily observed by putting a CRT monitor and a laptop next to each other for comparison.

- Improved efficiency. The efficiency of the polarizer, and overall display, are related to how much light it needs and therefore how much power it draws. Since
many of these displays will end up in portable computers, improved efficiency increases battery life.

- Added structures. For larger displays or special applications, additional specifications can be met by adding compatible 3M products.

The challenges specific to entering the high-end display industry are mostly market-based. It is a very difficult market to enter, with two Japanese corporations manufacturing around 90% of the iodine polarizer for high-end displays. Profit margins are relatively low in the display industry\(^\text{24}\), so the venture will be profitable only by selling large volumes or additional products.

4.3 Other Industries

Though 3M has focused on the automotive and high-end LCD markets for commercialization efforts of K-polarizer, polarizers have been introduced to a wide range of applications over the last eighty years, and most of these markets will still require sheet polarizers in the future.

The markets for these products are smaller, not under rapid growth, or lack the needs that make K-polarizer a solution for the automotive and high-end markets. As such, they are unsuitable for introducing K-polarizer. Upon successful commercialization, it is possible to make K-polarizer for other markets. The technology is well-suited for adapting to customer’s needs, being able to match the optics of everything from the very low-end of
iodine polarizers to the best in the same process by altering a select few process parameters (Table 1).

4.4 Challenges

Commercialization of any new technology brings inherent challenges of both business and technical nature, and the introduction of K-polarizer is no exception. While each target market has specific challenges, to be successful in either, technical challenges must first be addressed, including the change of the market with respect to new technology and the profitability of the current process.

Disruptive technologies are among the greatest concerns of successful commercialization of K-polarizer. Research and advances in display technology are fast-paced, and a change in the industry could close off many markets to polarizer manufacturers in general. Emissive displays, specifically OLEDs, pose a challenge to K-polarizer commercialization. OLED displays still require circular polarizers, but they will not require the brightness-enhancing film, which is used in almost all LCD displays, the best and most common of which is made by 3M. Until recently, OLEDs have been restricted in use to small, low content applications like cell-phones and car radios. Recent developments have allowed the use of OLED displays to grow. The first major commercial products are the Kodak LS633, the first consumer-release digital camera with an OLED display (2.2", 512 x 218 pixels)\textsuperscript{25} and the prototype 20" full color WXGA display from Chi Mei Optoelectronics\textsuperscript{26}. The success of these products indicates that OLED displays could be widely distributed and gain significant market share in the next
few years, at the expense of the polarizer industry. Despite the wide viewing angle and low power needs, OLEDs are still very expensive and less stable than LCD, so have not been widely adopted for displays. Should OLEDs become widely distributed for larger displays, 3M has less of an opportunity to sell brightness-enhancing layers in combination with and specifically for its K-polarizer.

Before K-polarizer can be commercialized, the manufacturing process must also be refined to make it more efficient and more profitable. Currently, the process takes place over several different machines. To sell this commercially, the machines must first be integrated, and the production rate will have to increase. Such changes will result in more material produced in a shorter time, requiring less handling and fewer operators.

5.0 Intellectual Property

In developing any new product for commercialization, relevant patents must be carefully checked to avoid future liabilities and to provide background when patenting any new processes, products, or applications that come about during development. Failure to do so can result in expensive lawsuits, licensing, or royalties as well as loss of revenue should the product be pulled from the market due to legal complications.

5.1 Concentration of Current Intellectual Property

The earliest filed patents for K-polarizer (Appendix A) expired some fifty years ago, and new ones have been filed as improvements in product or process are made. All relevant patents on K-polarizer have been filed for by the Polaroid Corporation of Cambridge,
Massachusetts and Dover, Delaware, and in recent years, by 3M Innovation Properties, of Saint Paul, Minnesota. All intellectual property associated with the K-polarizer and polarizer division of Polaroid was purchased in 3M’s acquisition of the polarizer division in 2000 (3M Press Box). During the acquisition, most personnel who were working with the K-polarizer development project stayed on with 3M, and they are a great repository of knowledge about the science and manufacturing of K-polarizer.

Many patents have been filed by other companies for the use of dichroic dye in polarizers. Most of the filed patents are from companies who make iodine polarizer, Pola-Techno, Sanritz Corporation, and Nitto-Denko Corporation, all of Japan. Fortunately, these patents cover different dyes, processes, or applications that distinguish 3M’s use of dichroic dyes. Specifically, 3M has sought to

- Use a dye of novel structure for polarizer applications. Most patents (Appendix A) have been filed for the specific use of azo compound dyes, which have a \( N=N \) chromophore in an aromatic system.
- Include the dye in a specific type of polarizer in a specific manufacturing step which is unique to 3M’s K-polarizer process.
- Alter only the color properties and absorption spectrum of the polarizer. The dye is not being used as a source of polarization and will not degrade the optical and durability qualities of the current product.

Based on these differences, 3M should be able to avoid licensing IP from other companies and should be able to file something of their own, should they choose.
5.2 Blocking Intellectual Property

Despite the fact that earlier patents on K-polarizer have expired, and the IP on the technology at those primitive levels is now in the public domain, no other manufacturer has tried to commercialize K-polarizer, for several reasons. K-polarizer has proved a very difficult product to make, and until recently, has not been optically competitive with iodine polarizers. Furthermore, the greatest challenge for competitors trying to take up the process lies not in making K-polarizer up to the current standards of iodine, but in knowing the next steps to take to bring it to the point it can be successfully commercialized. This presents technical difficulties as well as limitations based on knowledge – only people who have worked with the process recently have the knowledge of what steps have been taken and for what reasons to get the product where it is optically, and how to proceed without doing it at the expense of these characteristics. Since most people who have worked on K-polarizer in recent years are still working on it, the knowledge base for this is extremely limited, and exists almost completely within 3M.

5.3 Patent or Trade Secret?

In contrast to the patent craze that has hit other technical industries in recent years, the use of trade secrets is not uncommon in the display industry.

Owing to the cost, restrictions, and limited rights of patents, display manufacturers may maintain as a trade secret techniques that do not bring them significant advantages over their competitors, particularly if the methods cannot be derived by reverse-engineering
the final product. Trade secrets work best for ideas that bring competitive advantage by not being generally known. By not going through with the patent process, the inventor loses the opportunity to license the technology, and risks having a competitor develop the same technology independently and patent it. On the other hand, trade secrets can successfully protect methods and formulas for much longer than the 20 year patent in the United States.

In the case of K-polarizer, the initial patents on the technology were filed ages ago, in a technological time frame. Since then, patents have been filed pretty regularly as novel and patentable processes are added or modified to the process. Despite the expiration of older patents, the technology has not been picked up by competitors.

Recent work on improving the optics of K-polarizer has involved both forms of intellectual property. At least one patent was filed for a new method during the span of this project. The dichroic dyes, on the other hand, are being used in a process that they were never intended for and in a manufacturing step which differs from previously patented processes. The dye used would remain a trade secret. Though its manufacture might be patented by another corporation, the use of this dichroic dye is specific to the 3M K-polarizer process. This is facilitated by releasing only the necessary data about the material. Only the people who were actively involved in purchasing the dye know specifically where it comes from. At the plant in Norwood, Massachusetts, were K-polarizer is manufactured, researchers know only what the dye may have been intended for and a little bit about some functional groups, which were obtained by mass
spectrometry. Interestingly, the dye was originally developed for a completely different purpose, for which it did not need to be dichroic. However this property makes it an ideal material for inclusion in the K-polarizer, and has been shown to improve the color qualities of the final product, which could prove to be a resolution in the flat-panel display industry.

6.0 Conclusions

The increased market for LCD displays everywhere, and especially in the high-durability automotive and the high-end laptop and LCD television markets which are targeted by 3M for the commercialization of K-polarizer, means that K-polarizer can be introduced to a willing market upon completion of the technology development phase. Experimental results from processes run with dichroic dyes show near color neutrality without a compromise in \( k_o \), efficiency, or durability.

This new technology can be used to make polarizers to match even top of the line iodine polarizers, but with great advantages in durability which iodine will not be able to make up for, due to the instability of the potassium-iodine chromophore complex.

No other company manufactures K-polarizer, and there is no existing intellectual property to prevent 3M from commercializing the current process including the use of yellow dichroic dye.
## Appendix A. Relevant Patents

<table>
<thead>
<tr>
<th>Patent #</th>
<th>Date</th>
<th>Title</th>
<th>Abstract</th>
<th>Inventor</th>
<th>Assignee</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,973,834</td>
<td>1997, December 19</td>
<td>Method for the manufacture of a light-polarizing polyvinylene sheet</td>
<td>A method is provided for the manufacture of a polyvinylidene-based light polarizer (cf., a &quot;K Sheet&quot;-type polarizer). In one embodiment, the polyvinylidene chromophore of said polarizer is produced by the acid catalyzed dehydration of an oriented polymeric starting material, the acid catalyst being introduced in the method as a bonding agent used to secure the starting material to a carrier web (or other supporting substrate). Advantages of the method include reduced frequency of &quot;streaking&quot; and &quot;notching&quot;; good processing speed; and the ability to use a low acid concentration, resulting in a correspondingly low-corrosion processing environment.</td>
<td>Kadaba; Narenda S. (Newton, MA); Shah; Lort P. (Bedford, MA)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
<tr>
<td>5,666,223</td>
<td>1995, December 1</td>
<td>High-efficiency K-sheet polarizer</td>
<td>This invention relates to a new and improved light-polarizing sheet comprising molecularly oriented polyvinyl alcohol containing an oriented block segments of polyvinylene and said polyvinyl alcohol. In particular, the polarizing sheet comprises a polyvinylalcohol/polyvinylene block copolymer material wherein the polyvinylene segments thereof are formed by molecular dehydration of a sheet of polyvinylalcohol; said sheet of polyvinylalcohol/polyvinylene block copolymer material comprising a uniform distribution of light-polarizing molecules of polyvinylalcohol/polyvinylene block copolymer material varying in the length, n, of the conjugated repeating vinylene unit of the polyvinylene block of the copolymer throughout the range of from 2 to 24, the concentration of each of said polyvinylene blocks, as determined by the absorption of wavelengths ranging from 200 to 700 nm remaining relatively constant, the degree of orientation of said light-polarizing molecules, as measured by the spectral dichroic ratio, R.sub.D, of said blocks, increasing throughout said range with increasing length, n, of said polyvinylene blocks; said polyvinylene block concentration and said degree of orientation of said molecules imparting to said sheet a photopic dichroic ratio, R.sub.D, of at least approximately 45.</td>
<td>Bennett; Stewart (Concord, MA); Cael; John J. (Mendon, MA); Kadaba; Narenda S. (Chesnut Hill, MA); Trapani; Giorgio B. (Cambridge, MA)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
<tr>
<td>5,639,809</td>
<td>1997, June 17</td>
<td>Azo compounds and polarizing films using the compounds</td>
<td>The present invention provides a polarizing film having high heat resistance and a high degree of polarization and excellent optical properties by dyeing a polymer film with a novel azo compound represented by the formula (1) or (2)...</td>
<td>Matsuzaki; Yoritsuki (Kanazawaken, JP); Ot; Ryu (Kanazawaken, JP); Inai; Rohoko (Tokyo, JP); Takunuma; Keinuke (Kanazawaken, JP); Itoh; Hisato (Fukusuka-ken, JP)</td>
<td>Mitsui Toatsu Chemicals, Inc. (Chiyoda, JP)</td>
</tr>
<tr>
<td>5,286,420</td>
<td>1994, February 15</td>
<td>Production of light polarizing films</td>
<td>A process for the production of light-polarizing films containing polyvinyl alcohol, dichroic dye-producing components, optionally other dye-producing components, optionally additives, and optionally surface active compounds, wherein the films comprise two or more layers and said film layers have a sudden change in composition at the layer phase boundaries between at least two layers, and said layers are applied to a substrate by means of a multiple coater.</td>
<td>Claussen; Uwe (Leverkusen, DE); Krook; Friedhelm-Wilhelm (Odenthal, DE); Rothe; Eduard (Lohmar, DE)</td>
<td>Bayer Aktiengesellschaft (Leverkusen, DE)</td>
</tr>
<tr>
<td>Patent #</td>
<td>Date</td>
<td>Title</td>
<td>Abstract</td>
<td>Inventor</td>
<td>Assignee</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------</td>
<td>-------------------------------------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-----------------------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>5,071,906</td>
<td>1991, December 10</td>
<td>Polarizing film and process for the production of the same</td>
<td>A polarizing film comprising a uniaxially stretched film containing a polyvinyl alcohol having a degree of polymerization of at least about 2,500, and at least one polarizing agent selected from iodine and a dichroic dye, as well as a process for the production of the same. This polarizing film is superior in heat resistance and moist heat resistance to conventional films and has excellent optical properties, such as a high polarizing coefficient and transmittance.</td>
<td>Tanaka; Chikahumi (Kyoto, JP); Shirozawa; Masami (Kyoto, JP); Nakajinohara; Minowa (Kyoto, JP)</td>
<td>Unitika Ltd. (Hyogo, JP)</td>
</tr>
<tr>
<td>4,895,769</td>
<td>1990, January 23</td>
<td>Method for preparing light polarizer</td>
<td>A stainable polymeric sheet material adapted to the production of a light polarizer therefrom is provided by a method, according to which, a support sheet of amorphous polymeric material is uniaxially stretched in a first direction (at or above the glass transition temperature of the polymeric support material), a layer of polyvinyl alcohol (PVA) is coated from an aqueous PVA-containing composition onto the uniaxially stretched support material, and the PVA-coated uniaxially stretched polymeric sheet material is stretched along a second direction, at an angle within about ±0.6 degrees to a normal to the first direction of stretch. The method provides a material which can be converted, by incorporation of visible dichroism into the PVA layer, to a light polarizer which combines efficient light polarizing properties and good mechanical strength and resistance to fracture along the stretch directions.</td>
<td>Land; Edwin H. (Cambridge, MA); DiRocco; Anthony J. (Billerica, MA); Polizzotto; Leonard (Lowell, MA)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
<tr>
<td>4,818,624</td>
<td>1989, April 4</td>
<td>Stabilized light-polarizing material</td>
<td>Light polarizers stabilized against effects of temperature and humidity are provided by a silylation method whereby a polyvinyl alcohol light-polarizing sheet is treated with an organosilane and is bonded to the organosilane to the polyvinyl alcohol surface and to thereby silylate the surface thereof.</td>
<td>Downey, Jr.; John F. (Lexington, MA)</td>
<td>Polaroid Corporation, Patent Department (Cambridge, MA)</td>
</tr>
<tr>
<td>4,659,523</td>
<td>1987, April 21</td>
<td>Production of iodine stainable polyester polarizer film</td>
<td>A process for preparing an iodine stainable polyester polarizer film which comprises: (a) extruding a moving molten web of polyester film; and (b) quenching said moving web to solidify it in a substantially amorphous form; and (c) applying an anchor coating to at least a portion of the surface of said film wherein said anchor coating improves adhesion of polyvinyl alcohol to polyester film; and (d) applying a coating of a dispersed aqueous composition of polyvinyl alcohol to at least a portion of the surface of said film; and (e) stretching said moving web in a direction transverse to the direction of motion while heating said web at a temperature of from about its glass transition temperature to about 160 degree. C.; and (f) crystalizing said moving web by heating it to a temperature in the range of 130 degree. C. to 240 degree. C. without stretching said web; and (g) cooling said web to substantially ambient atmospheric temperature.</td>
<td>Rogers; John H. (Greenville, SC); Hopper; Michael J. (Taylors, SC); Martin; Michael R. (Greenville, SC)</td>
<td>American Hoechst Corporation (Somerville, NJ)</td>
</tr>
<tr>
<td>4,592,623</td>
<td>1986, June 3</td>
<td>Polarizing plate</td>
<td>A polarizing plate is disclosed, comprising a polarizing film and a protective layer bonded through an adhesive layer to at least one surface of the polarizing film, wherein the protective layer is a polyester film in which the minimum or maximum refractive index in a direction in parallel with the plane of the film is nearly equal to that in the direction of the film thickness and the retardation is at least 10 mum. On this polarizing plate, colored interference fringes are not formed at all even if it is looked at from any direction. Thus, the polarizing plate is suitable for use in the circumstance that it is exposed to the air, or in a display wherein a liquid crystal is used.</td>
<td>Nino Electric Industrial Co., Ltd. (Osaka, JP)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
<tr>
<td>4,591,512</td>
<td>1986, May 27</td>
<td>Method of making light polarizer</td>
<td>There is described a method for making visible range dichroic polarizer material comprising a uniaxially stretched film of polyvinyl alcohol stained with iodine and treated with a borating solution containing a zinc salt. The method comprises the steps of staining a uniaxially stretched sheet of polyvinyl alcohol and further stretching the stained sheet while it is being treated with a borating solution containing a zinc salt. High efficiency visible range dichroic polarizer elements having good neutrality, very high extinction and high transmittance can be made according to the method.</td>
<td>Racich; James L. (Natik, MA); Schulter; Norman W. (Lexington, MA); Trapani; Giorgio B. (Cambridge, MA)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
<tr>
<td>Patent #</td>
<td>Date</td>
<td>Title</td>
<td>Abstract</td>
<td>Inventor</td>
<td>Assignee</td>
</tr>
<tr>
<td>----------</td>
<td>----------------</td>
<td>--------------------------------------------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-----------------------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>4,292,370</td>
<td>1981, September 29</td>
<td>Moisture and temperature resistant polarizing lamination</td>
<td>A new moisture resistant polarizing lamination is disclosed which utilizes polypropylene as the protective layer. A polarizing film of polystyrene which has been stretched and treated with iodine is protected against moisture and structurally supported by at least one layer of polypropylene. The polypropylene is bonded to the polystyrene by adhesives which do not interfere with the polarizing effects of the lamination. The polypropylene may have a bonding layer already attached thereto which is covered by a protective film. The protective film is prevented from becoming secured to the bonding layer by a release agent placed between the protective film and bonding layer. The protective film is removed just prior to bonding of the polypropylene to the polystyrene alcohol. Use of polypropylene films that are 0.002 inch thick is disclosed. Polypropylene films of this thickness do not adversely affect the polarizing qualities of the lamination. The PVA polarizing film in a sandwich of polypropylene may be provided with one exterior adhesive layer for ease in securing the lamination in its desired final location.</td>
<td>Peikko; John A. (Whittier, CA)</td>
<td>Avery International Corporation (San Marino, CA)</td>
</tr>
<tr>
<td>4,166,871</td>
<td>1979, September 4</td>
<td>Iodine stained light polarizer</td>
<td>A visible range light polarizer is prepared by staining an oriented film of polystyrene alcohol with a solution containing iodine and its red light dichroism is enhanced by treating the stained film with a boric acid solution containing a zine salt.</td>
<td>Schuler; Norman W. (Lexington, MA)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
<tr>
<td>3,914,017</td>
<td>1975, October 21</td>
<td>K-sheet type polarizers prepared from polystyrene graft copolymers</td>
<td>K-sheet type polarizers are prepared from polystyrene alcoholic graft copolymers, said graft copolymers being obtained by a redox type grafting procedure utilizing certain transition metal cation catalysts.</td>
<td>Bedell; Stanley F. (Andover, MA); Taylor, Lloyd D. (Lexington, MA)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
<tr>
<td>2,674,159</td>
<td>1954, April 6</td>
<td>Process for the manufacture of light-polarizing sheets</td>
<td>This invention relates to a new and improved process for the manufacture of light-polarizing sheets. Objects of the invention are to provide a process for the production, continuously, of mechanically supported, thin, highly efficient, light-polarizing sheets or films, to provide such a process wherein the light-polarizing sheet or film comprises essentially a material from the class consisting of the polystyrene alcohols, the polystyrene acetals and the polystyrene ketals, and more specifically polystyrene alcohol which is molecularly oriented and which contains, distributed adjacent at least one surface thereof, the oriented dehydration product of polystyrene alcohol known as polystyrene; and to provide such a process wherein the polarizing sheet is of excessive thickness, has been treated with a cross linker and with a buffer so as to be highly resistant to the action of heat, moisture and sunlight, and wherein the polarizing sheet is bonded, as by an autogenous bond, to a transparent, mechanically strong, plastic backing comprising, preferably, a cellulose material.</td>
<td>Binds; Frederick J. (Cambridge, MA)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
<tr>
<td>2,554,850</td>
<td>1951, May 29</td>
<td>Heat resistant light-polarizing polystyrene borate film containing borax</td>
<td>This invention relates to a new and improved light-polarizing material and more specifically to an improved light-polarizing sheet or film of the type described in Patent No. 2,377,657, issued April 8, 1941, to Edwin H. Land. An object of the invention is to provide a light-polarizing sheet or film comprising a molecularly oriented polystyrene compound having incorporated therewith a dichroic complex of iodine and said polystyrene compound, and stabilized against moisture, ultraviolet radiation and heat.</td>
<td>Binds; Frederick J. (Cambridge, MA)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
<tr>
<td>2,445,555</td>
<td>1948, July 20</td>
<td>Light-polarizing polystyrene sheet containing polyvinyl compound-boric acid complex</td>
<td>This invention relates to a new and improved light-polarizing sheet comprising molecularly oriented polystyrene alcohol containing oriented polystyrene and having incorporated therewith a heat- and moisture-resistant complex of polystyrene alcohol and boric acid.</td>
<td>Binds; Frederick J. (Cambridge, MA)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
<tr>
<td>2,375,963</td>
<td>1945, May 15</td>
<td>Process of manufacturing light-polarizing material</td>
<td>This invention relates to a new and improved process for the formation of sheets of light-polarizing material. It is one object of the present invention to provide a process for improving the quality and properties of light-polarizing sheets or films of the type described in Patent No. 2,377,657, issued April 8, 1941, to Edwin H. Land.</td>
<td>Thomar; A. (Weston, MA)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
<tr>
<td>Patent #</td>
<td>Date</td>
<td>Title</td>
<td>Abstract</td>
<td>Inventor</td>
<td>Assignee</td>
</tr>
<tr>
<td>----------</td>
<td>------------</td>
<td>--------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>--------------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>2,306,108</td>
<td>1942, Dec 22</td>
<td>Method of manufacturing light polarizing material</td>
<td>This invention relates to a method of manufacturing light-polarizing material. An object of the invention is to provide a process for the production of a sheet or film of light-polarizing material consisting of a transparent plastic, having long molecules, and more specifically polyvinyl alcohol, with its molecules oriented to substantial parallelism, and which is differentially absorbing to components of an incident beam of light vibrating in different directions. A further object of the invention is to provide a process for decreasing the heat sensitivity and the water permeability of light-polarizing material of the character described.</td>
<td>Land; Edwin H (Cambridge, MA); Rogers; Howard G (West Newton, MA)</td>
<td>Polaroid Corporation (Dover, DE)</td>
</tr>
<tr>
<td>2,255,940</td>
<td>1941, Sept 16</td>
<td>Process for the formation of light-polarizing material</td>
<td>This invention relates to a new and improved process for the formation of sheets of light-polarizing material. An object of the invention is to provide a process for improving the quality of light-polarizing sheets or films of the type described in the copending application of Land and Rogers, Serial No. 271,814 filed May 4, 1939 now Patent No. 2,173,304.</td>
<td>Rogers; Howard G (West Newton, MA)</td>
<td>Polaroid Corporation (Dover, DE)</td>
</tr>
<tr>
<td>2,173,304</td>
<td>1939, Sept 19</td>
<td>Light polarizer</td>
<td>This invention relates to a light-polarizing material. An object of the invention is to provide a sheet or film of light-polarizing material consisting of a transparent plastic, having long molecules, and more specifically polyvinyl alcohol, with its molecules oriented to substantial parallelism, and which has been heat-treated to become differentially absorbing to components of an incident beam of light vibrating in different directions. A still further object of the invention is to provide a light-polarizing sheet or film which may be readily and efficiently laminated to glass or other supportin g elements, which is substantially unaffected by most organic solvents, by ultra-violet radiation, by temperature changes within ordinary limits, and which may be protected from the action of water.</td>
<td>Land; Edwin H (Cambridge, MA); Rogers; Howard G (West Newton, MA)</td>
<td>Polaroid Corporation (Cambridge, MA)</td>
</tr>
</tbody>
</table>
References


Recommended Reading


