Polarcor™ Polarizing Glasses

N. F. Borrelli and T. P. Seward III

Abstract

A history and review of polarizing glass, in particular Polarcor™ is presented. A description of the general process of making a polarizing glass, along with the physical phenomena involved is described. A brief review of the physical basis is also given. Some examples of the performance and applications are given

I History and background

The production of light polarizing materials in the form of plastic sheet is a well-known art. The production of glass polarizers is less well known. However, because plastic materials suffer for many applications because of their inherently low surface hardness, relatively high moisture susceptibility and limited chemical and thermal durability, all areas in which glass performance excels, glass is the material of choice for many optical applications and much effort has gone into developing all-glass polarizers.

Edwin Land, the inventor of plastic sheet polarizers and first to commercialize them (Polaroid brand products), also experimented with glass polarizers made by elongating (stretching) metal particles suspended in a glass matrix[1]. He reported unusual color effects as well as light polarization, but was apparently unsuccessful at producing a commercial glass-based polarizer product.

Stookey and Araujo, experimenting at Corning Incorporated (then Corning Glass Works), produced strips of polarizing glass based on elongated nano-particles of silver metal in glass and successfully explained the high degree of light polarization and the colors obtained on the basis of respective surface plasmon resonances of the conduction electrons in the asymmetric silver metal particles[2]. In particular, they explained how the location of the absorption bands depended on the aspect ratios of the elongated metal particles and the orientation of the polarized light field with respect to the elongation axis of the commonly aligned particles. Figure 1 illustrates this effect. The particle aspect ratios required to produce absorption maxima at various wave-

S&T Division, Corning Incorporated
Corning NY 14831 USA
E-mail : Borrellinf@Corning. com, Sewardtp@Corning. com.

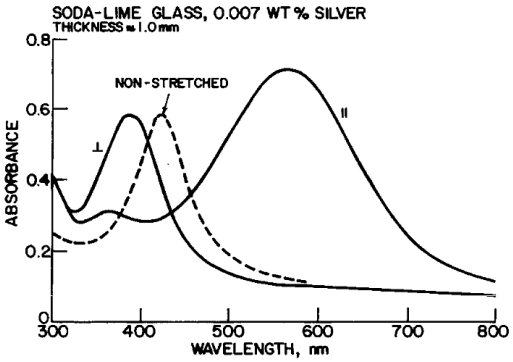

Figure 1 – Wavelength dependence of the absorption changes when the silver particles are stretched. The greater the elongation, the more the parallel absorption moves to longer wavelengths and the perpendicular absorption moves to shorter wavelengths. The spherical (non-elongated) particle absorbs most strongly near 400 nm.

lengths can be estimated using equations given in References[2, 3, 4], as described in section IV, below.

Stookey and Araujo's work initiated extensive studies of these phenomena at Corning, much of which has been reported in the open literature. For example, it was demonstrated that strong resonance absorption could be produced using copper or gold nano-particles, but the degree of polarization was limited by the contribution to the dielectric function of inter-band electronic transitions. This tends to detract from the desired conduction electron resonance condition. The optimum condition obtains from a material that essentially produces a free electron-like dielectric function that is Drude-like[5]. This is why base metals, e. g. , lead and bismuth, do not exhibit such resonance and consequently perform poorly as polarizers.

II New Process Development

As we will see in the later sections, the new idea that was proposed for making a polarizing glass was based on the Ag-halide-and Cu-halide-based photochromic glass systems[6, 7]. Elongation of such glasses under high stresses produced an elongation of the metal-halide phase and a weak polarizing effect when in the darkened state[8, 9].

The novel concept taken by Corning was that silver halide particles suspended in a glass matrix, as in typical photochromic glasses, could be thermo-chemically reduced to the metallic state[10]. Borrelli and Lo[11]showed that if the silver halide particles were elongated and aligned by a suitable mechanical process prior to the reduction step, elongated silver particles resulted after reduction, providing significant light polarizing effects (contrast ratio and transmission). That is to say much superior to that originally reported by Stookey and Araujo[2]. Moreover, as we will see later, this had the significant advantage of being achieved at much lower stresses.

III Description of new Method

Two practical methods for elongating the particles, namely drawing and extrusion[12] at a temperature above the strain point temperature, and two types of particulate materials, either a metal or a secondary phase that can be thermo-chemically reduced to metal, emerged from these studies. But to understand the difficulties in developing a commercial product (faced by Land, Stookey, Araujo), one must look at the polarization principles and the particle elongation process in some detail.

III A Principles : When glasses containing a dispersion of second-phase particles are elongated under a tensile load, the second-phase

particles tend to elongate into needle-like (ellipsoidal) shapes, aligned along the tensile axis. Such an arrangement of particles can give rise to unusual optical properties, including light polarization and birefringence[13]. If the second phase consists of small, elongated, light absorbing particles of refractive index different than the matrix glass, polarization effects result. This follows because the amount of light absorbed by the particles is proportional to the square of the electric field developed within the particles. This internal field depends on both the applied field and the electrical polarizability of the particle; however the polarizability of non-spherical particles depends on the direction of the applied field. It is this difference in polarizability that gives rise to the difference in absorption and, hence, produces a light polarizing material.

For cases where the absorbing particles' dimensions are comparable to or smaller than the wavelength of light, the degree of polarization can be calculated using light scattering theory, provided one knows the particle shape and dimensions and the optical constants of the metal involved. See for example, Reference[14].

III B Process : If the second phase particles are non-spherical as made (have one axis longer than the others), the particles can be aligned by the flow of the glass. On the other hand, if the particles are spherical or approximately equiaxed, the flow process must elongate the particles as well as orient them. In this case the requirements are that 1) the particulate material be deformable (either a liquid, a molten glass phase, or a deformable crystal) and 2) the elongating glass body (matrix) must impose on the particle sufficiently high deformation forces to overcome the surface tension forces tending to maintain the spherical shape and to deform the particle (via viscous flow if it is a liquid or glass, or via dislocation or vacancy motion if it is a crystal). These requirements are discussed in References[15, 16].

With small enough silver particle sizes, excellent polarization with acceptably low light scattering can be achieved. However the smaller the particle sizes, the greater the restoring forces due to surface tension and the more difficult it is to elongate the particles[15].

III C Surface tension and elongation forces : Experience has shown that much greater redraw stresses (often in excess of 10, 000 psi) are required to elongate silver metal particles of the size needed for good polarization than are required for elongating silver halide particles of comparably useful sizes (a few thousand psi). This is of particular concern for the high degree of elongation needed for NIR polarization and is the primary reason that Polarcor manufacturing uses a two-step process: first precipitate and elongate silver halide particles, then chemically reduce the silver halide to silver metal in a hydrogen gas environment. The requirement for high redraw stress and the difference in stresses required to elongate silver metal and silver halide can be explained in terms of surface tension.

Surface tension (interfacial energy) tends to minimize the surface area of a liquid (or molten glass) droplet, causing it to achieve spherical shape. It also produces an internal pressure within the droplet, given by $P = 2\gamma/r$,

where γ is the surface tension and r the radius of the sphere. If the droplet is distorted from its spherical shape, the pressure beneath any point on the surface will be given by $P = 2\gamma (1/r_1 + 1/r_2)$, where r_1 and r_2 are the radii characterizing the curvature of the surface at that point.

A droplet of silver halide, such as found in photochromic glasses and Polarcor products, has a surface tension of about 150 erg/cm^2, a radius of about 10 nm and, according to the pressure equation above, an internal pressure of about 4, 500 psi. Therefore, it is understandable that viscous forces of this order of magnitude are needed to significantly elongate such particles by redraw or other techniques.

The air–metal surface energy of noble metals is about an order of magnitude higher that that for silver halides, so even allowing for the metal to wet the glass, the glass–metal interfacial tension is likely still considerably more than that for silver halide and therefore correspondingly higher deformation forces are required to deform a similarly sized particle.

Another factor favoring the elongation of silver halide over silver metal is that at the deformation temperatures used in drawing or extrusion (temperatures near the softening point of the glass) the silver halide particles are fluid droplets and will elongate (deform) in proportion to the elongation (deformation) of the glass matrix. Metal particles, on the other hand, are in the solid crystalline state and must elongate via dislocation motion or atomic diffusion, thus elongate more slowly than the host glass.

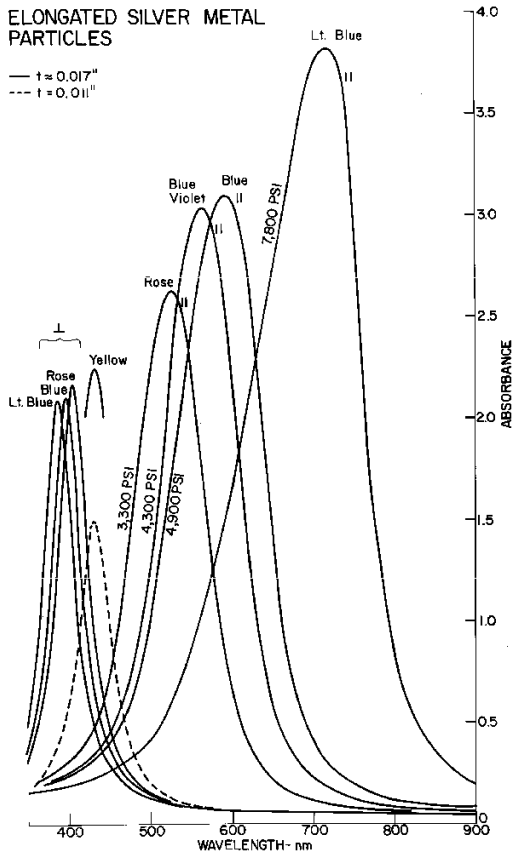

Figure 2 – Wavelength dependence of absorption of elongated silver metal particles in a soda–lime–silica glass as a function of drawing stress. Higher stresses produce greater elongation. The colors noted are those seen when two similar glass samples are crossed and viewed in white light. (t indicates glass thickness.)

Figures 2 and 3 show absorption bands developed in drawn glasses containing silver and hydrogen–reduced silver halide, respectively. The higher draw stresses required for the silver particles are also shown. Since 1000 psi is often considered a practical maximum engineering design stress level to avoid breakage, the silver halide–containing material has a clear manufacturing advantage.

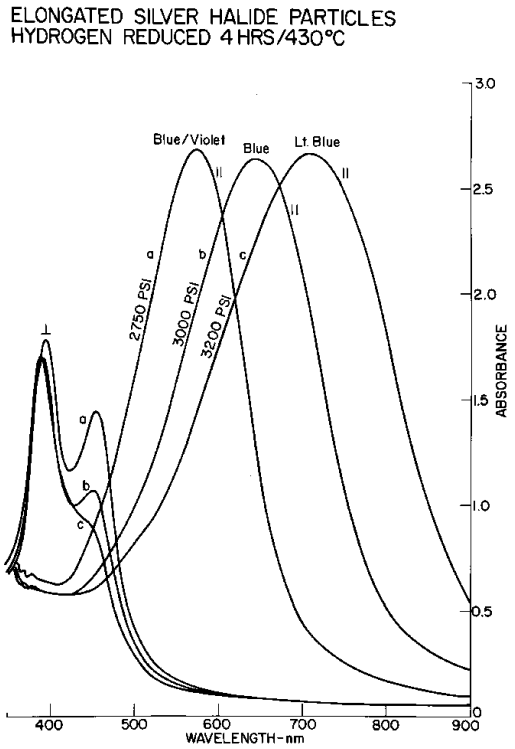

Figure 3 – Wavelength dependence of absorption of elongated silver metal particles in a hydrogen–reduced silver–halide–containing borosilicate glass. The colors noted are those seen when two similar glass samples are crossed and viewed in white light. The smaller absorption peaks near 470 nm are presumed due to small spherical silver particles also produced during the reduction process.

The hydrogen–reduced metal halide approach has another inherent advantage : The amount of light absorption and contrast (ratio of parallel to perpendicular absorption) can be controlled by the degree of hydrogen reduction, as shown in Figure 4.

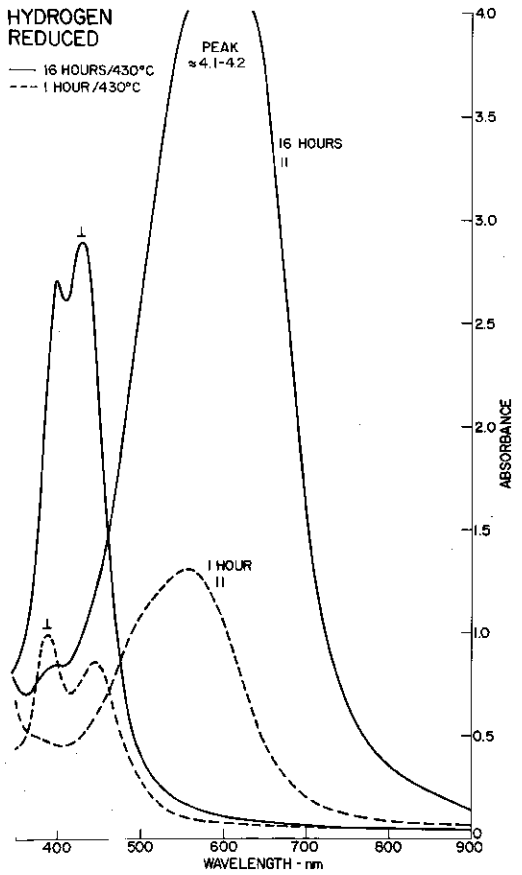

Figure 4–Wavelength dependence of absorption of elongated silver metal particles in a hydrogen–reduced silver–halide–containing borosilicate glass as a function of degree of hydrogen reduction.

IV Theory

According to light scattering theory, if the metal particles have dimensions small compare to the wavelength of the light and are spaced sufficiently far apart to be non–interacting, the absorption cross–section per particle may be written in terms of the complex dielectric constant $\varepsilon_c = \varepsilon_1 - i\varepsilon_2$ of the particle material[14] :

$$C_{abs} = (2\pi V n_0^3 / L^2 \lambda) \cdot (\varepsilon_2 / \{[\varepsilon_1 + n_0^2 (1/L - 1)]^2 + \varepsilon_2^2\}) \quad (1)$$

where V is the volume of the particle, n_0 is the refractive index of the glass matrix, λ is the wavelength in free space, and L is the electric depolarization factor appropriate for the particle geometry and orientation with respect to the applied field. Whenever one can approximate the particle geometry by a prolate ellipsoid (of axial ratio r = a/b), the L values can be found analytically or in tables[17].

For the case of absorbing dielectric particles in glass, such as second-phase glassy phase particles, ε_2 can be derived directly from the measured absorption coefficient of that second phase. In the case of metal particles, which are opaque to light, the approach to calculation must depend on published optical constants for the metal in question, or, for good conducting metals like silver, gold and copper that approximate "free electron" behavior, one can fit the experimental data to a second or third order equation in wavelength. For these materials, a resonant absorption occurs at a wavelength for which the first term in the denominator of Equation 1 goes to zero, i. e. , when $\varepsilon_1/n_o^2 = (L-1)/L$. This wavelength obviously depends on the optical constants of the metal, the refractive index of the glass, the particle geometry, and the polarization direction of the light (through the depolarization factor L). A wide range of colors can be produced by varying the size and aspect ratio of the particles and the polarization direction of the viewing light.

Based on the free electron theory[5], the complex dielectric constant of bulk silver metal can be written in the approximate form

$$\varepsilon_c = \varepsilon_1 + i\varepsilon_2 = \varepsilon_0 - A\lambda^2 + iB\lambda^3 \qquad (2)$$

Substituting Equation 2 into 1,

$$C_{abs} = (2\pi V n_0^3/L^2) \cdot (B\lambda^2/\{[\varepsilon_0 - A\lambda^2 + n_0^2(1/L - 1)]^2 + B^2\lambda^6\}) \qquad (3)$$

which, when plotted as a function of wavelength gives a Lorentzian line shape.

The authors and co-workers[18]have found a good fit to published experimental data for the optical properties of bulk silver to be

$$\varepsilon_1 = 5 - 55\lambda^2$$
$$\varepsilon_2 = 0.06 + 27\lambda\exp(-29\lambda^2) + 1.6\lambda^3$$

where λ is expressed in μm. The first terms in ε_1 and ε_2 can be interpreted as the wavelength-independent contribution of bound electrons; the second term in ε_2, important only in the ultraviolet (for silver), represents the onset of inter-band transitions; and the last term in each is the conduction electron contribution. So, in the near infrared spectral region, $\varepsilon_0 = 5$, A = 55 and B = 1.6.

The resonant absorption occurs when the first term in the denominator of Equation 3 is zero. For a spherical particle of silver in a glass of index 1.5, L = 1/3 putting the resonant absorption at about 416 nm. The wavelength of maximum absorption, λ_{max}, depends on the degree of particle elongation and the orientation of the polarized radiation through the electrical depolarization factor L. For particles of ellipsoidal shape, L ranges from 1/3 to zero for the parallel direction and 1/3 to 1/2 for the perpendicular orientation.

The following are SEM images of the particles stretched to various degrees corresponding to different resonant wavelengths as noted.

V Performance and Applications :

In the early 1980 s, the need for glass near-infrared polarizers became apparent and Corning's Polarcor™ products were developed[3, 19, 20, 21, 22, 23]. Figure 6 shows near infra-red transmittance spectra of polarizing glasses containing

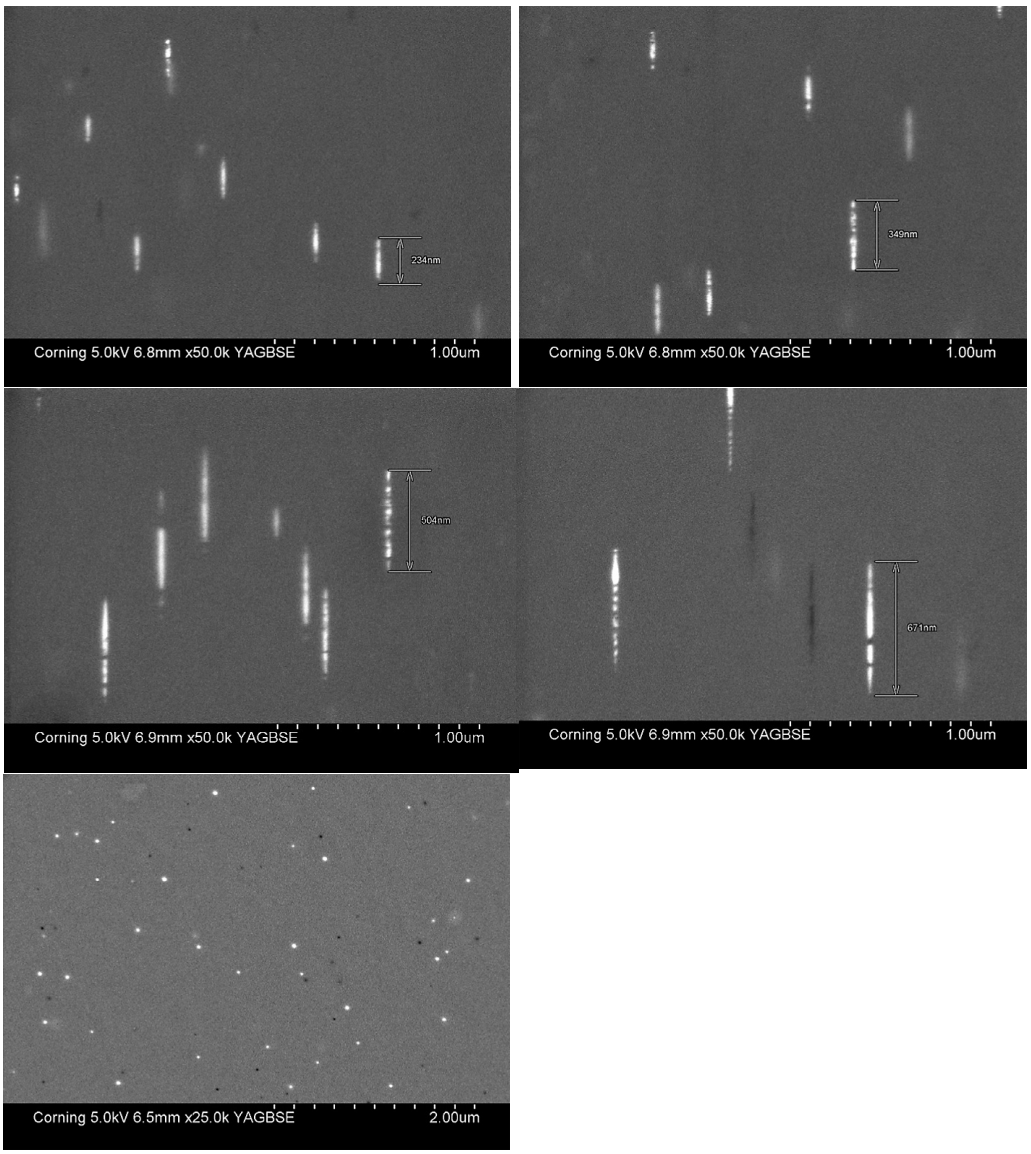

Figure 5 ; Top series clockwise ; wavelength (particle length, aspect ratio), 633 nm (234 nm, 2. 7), 900 nm (349 nm, 3. 5), 1550 nm, (671 nm 7. 7), 1310 nm (504 nm, 5. 8). Bottom ; width dimension (87 nm)

hydrogen–reduced elongated silver halide particles.

The major application of such IR polarizing glasses is for polarization dependent optical isolaters[24] for the telecommunication industry. In particular they are used for eliminating feedback into the laser diode sources. Typi-

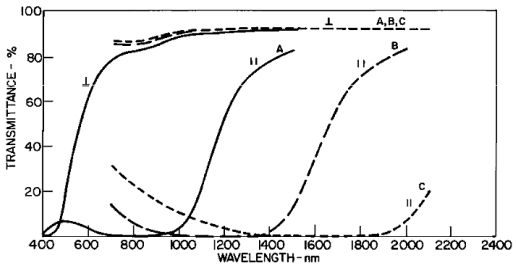

Figure 6 – Near infrared transmittance spectra of polarizing glasses containing hydrogen–reduced elongated silver halide particles (from Reference 3)

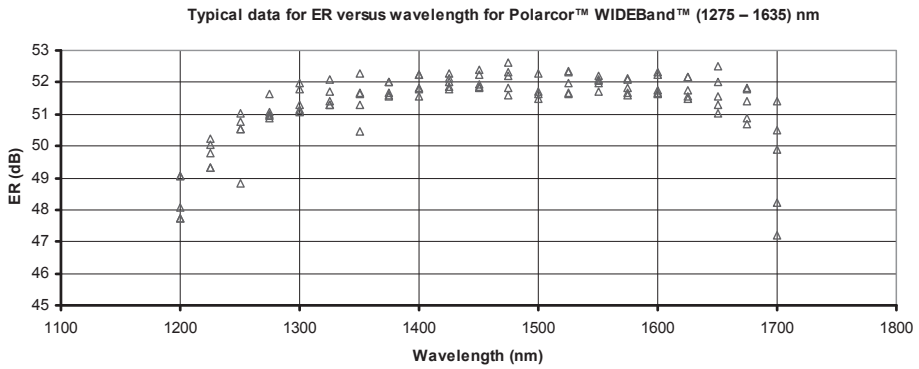

Figure 7：Contrast in db vs. wavelength for Polarcor™ wide band polarizer.

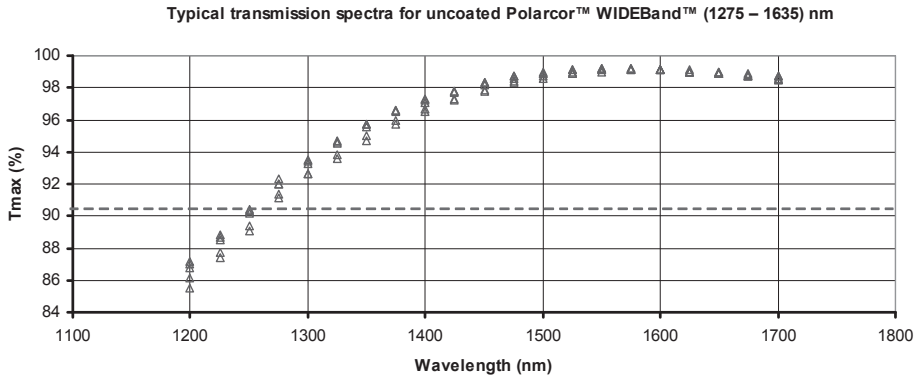

Figure 8：Transmission vs. wavelength including antireflecting coatings

cally for the application greater than 50 db rejection is required. Also the loss must be minimal, ＞98% transmission, at the operating wavelength including antireflecting coatings.

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