A Thesis Presented to

The Faculty of Alfred University

CREATING ECONOMIC PHOTOSENSITIVE GLASS BY ION EXCHANGE

Andrew J. Lanphere

In Partial Fulfillment of

the Requirements for

The Alfred University Honors Program

May 2013

Under the Supervision of

Chair: Dr. William LaCourse

Committee Members:

Dr. Alexis Clare

Dr. S.K. Sundaram

ACKNOWLEDGEMENTS

I would like to offer my sincere thanks to everyone who has offered me assistance and instruction over the course of this research project. First and foremost I would like to thank Dr. LaCourse not only for being an excellent professor and my advisor for this project in particular but also for his guidance over my four-year stay as an Alfred undergraduate. Thank you for your help with my research and for the prodding and suggestions when I didn't know where to go next. Thanks to Dr. Alexis Clare for everything you've taught me in the classes I took from you, and especially for unlocking the lab for me nearly every time I needed to do work. Further thanks to Dr. Scott Misture and Victoria Blair, for the use of the specialty UV lamp and the training in the use thereof. Finally, thanks to all of the people I have met and the friends I've made during my time at Alfred, who made it the incredible experience it was.

HONORS INTRODUCTION

Glass As A Material

Since its discovery thousands of years ago, glass has been used by humans for all manner of purposes. Glass possesses a unique set of material properties, from its transparency to its deceptive physical strength. Glass is inert to most chemicals, making it the perfect material to store everything from food to sensitive compounds such as vaccinations and medicines. Glass is very strong, at least theoretically, and advances are constantly being made to improve this strength. Eventually, the potential exists for glass to surpass materials like steel in terms of toughness and durability. Glass is also an electrical insulator and responds negligibly to magnetic fields, making it a good substrate for printed circuits and other microelectronic applications. However, glass' most useful properties are its optical properties. There is no other material that exhibits glass' transparency while also being rigid, durable, and shapeable. Not only is glass transparent, but it can also be nearly any color. The opacity and reflectivity can also be selectively altered by coatings or changes to the composition. This thesis looks at one way of manipulating these properties: the photochromic effect.

Photochromic Glass

Photochromic glass (also called 'photosensitive' glass) is a specialty glass that undergoes a color change when exposed to ultraviolet radiation. This effect occurs due to the presence of gold or silver in the glass composition. When the glass is melted, charged ions of gold or silver become distributed throughout the glass structure. This glass looks like a normal, uniformly transparent and uncolored piece of standard glass at this point. When the glass is exposed to UV light, however, a reaction occurs. The UV radiation promotes an interaction between the metal ions and another element in the glass called a sensitizing agent. Typically, this sensitizing agent is cerium. When given energy by UV radiation, the sensitizing agent donates an electron to the metal ion, reducing it to an uncharged, neutral atom. The glass is now ready to be colored.

Because it is neutral, these atoms are no longer bound tightly into the glass structure. This means that it takes very little energy to cause the atom to move around through the structure. The irradiated glass is heated, and this heat gives the atoms the energy required to do just that. The atoms begin to come together and merge into larger particles. As these nano-particles grow, they eventually reach a size that lets them interact with visible light. This causes certain wavelengths of light to scatter off the nano-particles, resulting in a color change. The glass turns a purple color if gold is used, and a brown color if silver was used. The amount of color change is related to the amount of UV exposure and the length of the heat treatment.

Motivations

Photosensitive glass has a few interesting applications. First, if a mask or a stencil is laid over the glass before it was irradiated, the color will only form where there were holes in the stencil. This allows for interesting patterning to be created, for artistic purposes and photolithography. A photographic negative used as a mask, for instance, results in a developed photo in the glass. However, there are more applications than that. The glass can be made to crystallize around the nano-particles, which makes that part of the glass especially vulnerable to acid. This allows for extremely specific chemical etching. By using a stencil of very high detail in combination with this crystallization, it is possible to etch very fine patterns into glass. This has applications in the chemical, biomedical, and pharmaceutical industries, where tiny channels could be used to test chemical reactions and controlled interactions using tiny amounts of chemicals.

However, there is not much work being done with photosensitive glasses because they are expensive. They require gold or silver as raw materials, which are very expensive. If the cost could be brought down, more expansive work could be done on their applications. This thesis is an investigation into one possible way to do just that.

Project Description

The best way to reduce the cost of photosensitive glass would be to reduce the amount of silver or gold required. Not only is it expensive it is generally also wasteful, because most of the uses of photosensitive glass use the surface layer only. An alternative would be to use ion exchange to place the silver or gold into the glass post-forming, so the only metal ions present in the glass will be at the surface. Ion exchange works by applying a solution to the glass surface that contains silver or gold. The glass is then heated. Metal ions move down into the glass surface, replacing sodium ions that move out. Over time, this builds up a layer that has enough silver or gold for the color change to occur, but using much less of the expensive metals.

Additionally, if the glass being used as the substrate is something like a soda-lime-silicate float glass, this cost can be reduced even further. Soda-lime-silicate glass is preferable because it is mass-produced, readily available, and very cheap. This thesis examines the viability of soda-lime-silicate glass as a substrate for ion exchanged photosensitive glass. Silver was the metal of choice due to its lower cost.

Experiments

A clay slip containing 2% silver nitrate was applied to seven sets of float glass samples. The samples were heat treated to speed up the ion exchange process, cleaned, and heat-treated a second time to relieve any stress in the glass created by the exchange. Next, the glass samples were irradiated under 500W of ultraviolet light to reduce the silver to neutral atoms. Finally, the irradiated glass was heat treated a third time to allow the nano-particles to form. Some of the samples were etched with hydrofluoric acid to remove tin from the surface of the glass, which is present from the float glass forming process and occasionally interferes with the photochromic process.

Results

The first sample set came out of the annealing treatment already colored. The silver was reacting with tin present in the glass, reducing too early. The second and third sample sets also performed similarly, not responding to the UV irradiation and coloring at the wrong time. It was determined that the silver was still reacting to the tin in the surface. The next four sample sets were etched with hydrofluoric acid to remove surface tin. However, this left the glass with no sensitizing agent and the coloration did not occur at all. This, unfortunately, means that float glass is an insufficient substrate for this process. With tin present in the glass, the coloration occurs at uncontrollable times. With the tin removed from the glass, the coloration does not occur at all. The next step is to find other mass-produced glasses that might work as substrates. Melting a custom composition might result in a more receptive glass, it would defeat the overall goal of reducing the cost of the finished product. Ion exchanged photosensitive glass is certainly still possible, but soda-lime-silicate float glass will not be the method we use to do it.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

ABSTRACT

Unaltered soda lime silica float glass plates were cut into 1”x4” samples. These samples were coated with a kaolin slip containing $AgNO_3$ and KNO_3. These glasses were heated to promote ion exchange, then heated again to equilibrate both stresses and the Ag concentration in the surface layer. Some samples displayed a high degree of undesirable coloration after this process. Additional samples were etched with 10% hydrofluoric acid to remove surface tin and heat-treated, these samples showed no coloration. The heat-treated samples were then masked and irradiated under a 500W ultraviolet lamp to reduce the silver and annealed a third time to promote coloration, with varying success.

I. INTRODUCTION

The physical properties of glass make it a valuable and useful material in a great range of industries. It is generally chemically inert, mechanically durable, electrically insulating, and transparent. It is used for containers, insulation, windows, communications, and much more. This research is concerned with manipulation of the optical properties of glass.

A. Photosensitive Glass

Glass that undergoes a color change when exposed to UV radiation is known as photosensitive glass. This specialty glass was first created in the mid-1900s by Armistead and Stookey at Corning Glass Works in Corning, NY [1-3]. Since then, it has been the subject of study by many different authors [4]. There are multiple methods of making photosensitive glass, but most of them rely on gold or silver as an additive to the glass composition. Gold or silver is added to the melt along with a sensitizing agent, typically cerium[1], which acts as a reducing agent to the gold and silver. Antimony, arsenic, and copper oxides can also serve as sensitizers[1]. The resulting melt is then formed into the desired geometry, typically flat sheets. This glass now has silver or gold ions distributed throughout it. When exposed to ultraviolet radiation, the metal ions react with the sensitizing agent, gaining an electron and reducing to their neutral metal state. The resulting atoms are very mobile. With heating to promote atomic movement, these atoms begin to agglomerate into nano-particles within the glass structure. With sufficient growth, these colloidal nano-particles interact with light in the visible spectrum, causing coloration of the glass.

Using masks or stencils over the glass during the irradiation process can result in patterns of colored and clear glass. The accuracy and clarity of these images is very high, to the point that a photographic negative used as a filter will result in a developed image within the glass.

B. Ion Exchange

Most photosensitive glasses studied and produced so far contains some amount of silver or gold as a raw material in the melt. Additional constituents have been studied in some detail by Kawamoto, Kikuchi, and Kimura[4], among others. However, using silver or gold as a batch ingredient is not only very expensive but is also wasteful; most of the uses of photosensitive glass only use the effect at the surface layer. Any metal ions in the bulk of the glass are unnecessary at that point. An alternative would be to introduce the silver or gold post-forming. The simplest way to do so is by ion exchange. A liquid solution or clay suspension containing the desired ions is placed on the surface of the glass. These metal ions begin to exchange with sodium ions from the glass surface. At room temperatures this process is very slow, but heat treatments at higher temperatures will accelerate the process and introduce the required concentration in a reasonable timeframe. Once the ion exchange is complete, the glass is heat treated to relieve any stresses in the glass and also to equilibrate the concentration of silver or gold in the surface. This is to reduce irregularity in the concentration that may have arisen from uneven coating with the ion solution.

C. UV Irradiation

The exposure of photosensitive glass to UV radiation is the step that facilitates the color change. Irradiation of the silver or gold ions in the glass causes the metal ions to capture an electron from the sensitizing agent and reduce to neutral metals. The degree to which this happens is dependent on the intensity of the radiation and the duration of exposure. Any masking of the samples for creating an image with the color change also takes place at this time.

D. Heat Treatments

Irradiation alone will not cause any color change in the photosensitive material. The glass must be heat treated in order to give the metal atoms enough energy to move through the glass. These atoms move together, agglomerating into nano-particles of gold or silver. The size and density of the nano-particles, and thus the amount of coloration, have a few controlling factors. Increased irradiation time reduces more of the metal, increasing the amount of atoms available to form into nano-particles. Additionally, higher temperatures and longer treatment times will allow more nano-particles to form and grow larger, darkening the color. In general, heating to just below T_g allows for good mobility and sufficient coloration after a short time. For a standard soda-lime-silicate (SLS) glass, T_g is approximately 560˚C.

E. Etching

When looking for alternatives to specialty glass compositions to use as a substrate, float glass seems ideal. It is readily available, cheap, and flat. However, due to the float glass process, one side of each sheet contains a high concentration of tin. This causes a problem for the photosensitive process. Tin acts a powerful reducing agent for silver ions, and easily interacts with the diffusing silver ions during the ion exchange process. The result is a premature and undesirable coloration that we do not have control over. This can be partially solved by removing the tin from the surface using acid. The acid bath contained 10% HF, used to remove the outer surfaces of the glass, removing the tin and other surface glass components. With the tin removed, ion exchange can take place without the interference of tin.

F. Objective

The goal of these experiments is to determine if unaltered soda-lime-silicate float glass can be used as a substrate for creating photosensitive glass by the ion exchange process. Float glass is highly desirable, being very commonly produced and available in large quantities at low prices in flat sheets. Silver was chosen as the exchanging metal, due to gold's much greater cost. Using ion exchange allows the use of much smaller quantity of silver to obtain the desired effect. Using float glass as a substrate removes the time-consuming and expensive extra steps of melting a specialty glass to receive the silver. Additionally, the ion exchange process can be performed at much lower temperatures and therefore lower energy requirements than melting glass. The long-term goal is to find the cheapest, most readily available composition that will accept the exchange process and allow a more economic means of production of this specialty glass.

II. EXPERIMENTAL

A. Base Glass

The glass used in this experiment commercial soda-lime-silicate float glass 2mm in thickness. This glass came in 4”x4” squares which were cut into four samples per square at 1”x4”. These samples were divided up into seven sample sets of three plates each that received a variety of subsequent treatments.

B. Silver Solution

The solution used to deliver the silver ions to the glass was a kaolin slip saturated with silver nitrate and potassium nitrate. The slip contained 2 wt. % $AgNO_3$ and 98 wt. % KNO_3.

The tin side of the float glass was identified by applying a small dab of slip to one face and heating the plate at 500°C for half an hour. This caused an immediate and distinct color change as the silver reacted with the tin in that face, identifying it as the tin side.

In order to get an even coating on the glass plates, the samples were dip coated and the slip on the tin side wiped off with a damp sponge and then dried with paper towels. This was done to minimize the chance of an accidental reaction with the tin face. All samples were kept orientation-preserved throughout all tests.

C. Hydrofluoric Etching

Adding the etching step was not included in the original procedure, but after the results of the first three sample sets it was decided to add it to see the effects. The acid bath contained hydrofluoric acid diluted with water down to a 10% acid solution. The samples were then soaked in the bath for varying lengths of time, given below in Table I.

Table I. Etch times for 7 sample sets of SLS glass.

Sample Set	**Etch Time (hours)**
1	0
2	0
3	0
4	0.5
5	0.5
6	1
7	1

D. Ion Exchange Heat Treatment

All seven sample sets were coated with the 2% $AgNO_3$ solution and then heated to 475˚C. The samples were held for one hour to allow the silver plenty of time to exchange into the glass, replacing sodium ions. Some potassium moves into the glass as well, but silver exchanges preferentially over potassium and the end result is a significant concentration of silver ions in the glass surface. The samples were allowed to cool slowly to room temperature before being washed to remove the dried slip.

E. Post-Exchange Anneal

Once the exchange was complete and the samples cleaned, each sample set was annealed to reduce any stresses that may have been induced by the ion exchange process and unify the distribution of silver across the surface. The specific treatment times and temperatures of each sample set is given by Table II, below.

Table II. Heat treatment of 7 sample sets of SLS glass, post ion exchange.

Sample Set	Anneal Time (hours)	Anneal Temperature (°C)
1	14	510
2	4	400
3	6	400
4	4	400
5	6	400
6	4	400
7	6	400

F. Irradiation and Coloration Heat Treatment

Once the samples were annealed, they were masked with electrical tape to expose a band of the exchanged glass to the UV radiation. If the process was successful, a band of color would develop in this exposed region and not in the region covered by the mask. An example of this is shown in Figure 1.

Figure 1. Masked samples from sample set 2, pre-irradiation.

The masked samples were all irradiated for one hour under 500W of UV light, with the exception of sample set 1, which was not irradiated. Following irradiation the mask was removed and the samples were heat treated a third time. The samples were held at 550°C for half an hour to promote the agglomeration of any neutral silver that was formed by the irradiation process.

III. RESULTS & DISCUSSION

A. Ion Exchange

The test spot used to determine which side was the tin side showed significant darkening, signifying that the amount of silver in the solution was more than sufficient to produce coloration. Each of the seven sample sets came out of the furnace showing little to no coloration, as expected for exchanging on the tin-free side. There were small spots of color on the edges, but this was a result of the slip leaking over the edge of the plate and reacting with the tin side rather than coloration of the tin-free side.

B. Post-Exchange Anneal

Sample set 1 was annealed overnight at 510°C, and came out of the furnace significantly colored. Given the similarity in appearance to the tin-side test sample, it is suspected that the heat treatment was too long and too high a temperature. The treatment gave the significantly mobile silver enough time to meet and react with the tin present in the glass. The result of this can be seen in Figure 2, below.

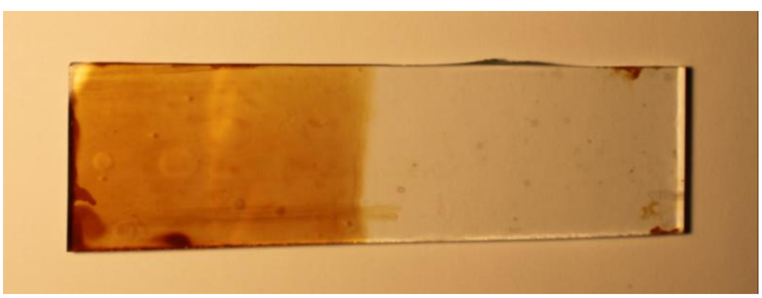

Figure 2. Sample set 1, post annealing.

The heat treatment schedule was revised to a lower temperature and a small variation in dwell time. Sample sets 2 and 3 still darkened during this process, and this prompted the decision to etch off the surface tin to see if that would prevent the early coloration. Sample sets 4 through 7 did not display any coloration as a result of the annealing heat treatment, as desired.

C. Irradiation and Coloration Heat Treatment

All six sample sets that were irradiated received 1 hour of irradiation under 500W of UV light, then were heated to 550°C and held there for 1 hour. Sample sets 2 and 3 were somewhat darkened by the annealing treatment, but they were irradiated to see if the coloration could be pushed further in a controlled fashion. The results of this are shown in Figures 3 and 4, below.

Figure 3. Sample set 2, post irradiation and heat treatment.

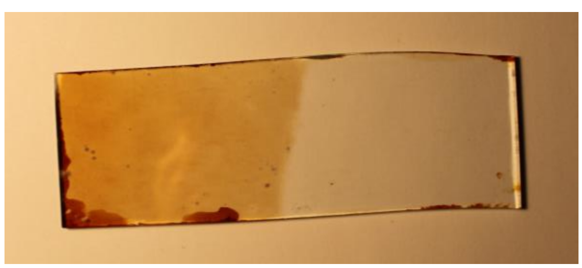

Figure 4. Sample Set 3, post irradiation and heat treatment.

The glass did darken in color, but it did so uniformly as opposed to only in the masked area. The best conclusion is that the silver was reacting too strongly to tin present in the glass as opposed to being reduced in a specific area by the UV light. Ideally the other sample sets would not have this problem, since the tin in those samples had been removed by the HF etching. The results are displayed in Figures 5 through 8, below.

Figure 5. Sample set 4, post irradiation and heat treatment.

Figure 6. Sample set 5, post irradiation and heat treatment.

Figure 7. Sample set 6, post irradiation and heat treatment.

Figure 8. Sample set 7, post irradiation and heat treatment.

These samples did not exhibit the uniform darkening of the previous sample sets. Instead, they did not change color by any significant degree. Since other samples were exchanged the same amount and received the same heat treatments but still colored, it can be concluded that the amount of silver was not the cause. It is more likely that the lack of tin in the samples left the silver with no electron source and therefore no way to color regardless of silver content.

IV. CONCLUSIONS

These experiments represent a successful evaluation of float glass as a photosensitive substrate. Several aspects of float glass make it a seemingly ideal candidate for economic, ion exchanged photosensitive glass. It is very low cost, very easy to obtain in large quantities, and requires no additional processing to use. However, the tin present in float glass proposes too much of an issue with the control of coloration. Even exchanging on the tin-free side results in a color change before UV exposure. This suggests that there may be tin even in the top surface, but that might be unique to this particular float glass manufacturer. Regardless, any amount of tin present in the glass seems to result in an uncontrolled color change.

However, etching away the tin gives the opposite problem. In the etched samples, the silver will not react even when present in sufficient quantities. Lack of a sensitizing agent to promote reduction means that float glass is an insufficient substrate both with and without tin present. Either the coloration occurs in an uncontrolled manner or does not occur at all. The goal of ion-exchanged photosensitive glass is certainly still within reach, but float glass will not be the method used to achieve it.

V. SUGGESTIONS FOR FUTURE WORK

The primary direction for future work on this project is an expanded search for other production glass compositions that could function as inexpensive substrates. The ideal next candidate would contain an element like cerium, to test the behavior of ion-exchanged silver with a more controllable sensitizing agent and additionally would contain no tin. Though it would be fairly straightforward to create a composition specially designed to receive the ion exchange treatment, this is less desirable. In the interest of minimizing the final cost of the product, finding a mass-produced composition that accepts ion exchange is a much better solution. This could provide the critical aspect, control over the degree and timing of coloration, without expensive batching and melting.

VI. REFERENCES

1. O'Leary, T.G., "Method of Making a Phototropic Glass Article", US Pat. 3306833, (1967)

2. Stookey, S.D., "Photosensitive Glass", US Pat. 2515275, 4 (1950)

3. Armistead, W.H., "Silver-containing Photosensitive Glass", US Pat. 2515936 3 (1950)

4. T.Kawamoto, R. Kikuchi, Y. Kimura, "Photosensitive glasses containing silver chloride," Physics and Chemistry of Glasses, 17[2] 23-26 (1976).