A Short History of Photosensitive Glass Patents

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Received: January 00, 2015 Revised: March 00, 2015 Accepted: March 00, 2015

Abstract: The development of photosensitive glass (PG) has a remarkable history since its first commercial discovery in the 1940s. The manufacturing of PG is one of the most widely reported methods for special glass manufacturing. PGs are capable of forming permanent photographic images when subjected to light, providing security, high quality and productivity. The first *U. S.* patent about photosensitive glass was filed on December 8th, 1943, and published July 18th, 1950, by Stanley Donald Stookey. A historical perspective about photosensitive glass represents an important step for future applications. PG has been considered one of the most interesting research areas with potential industrial applications. A number of companies and institutions have explored the usefulness of such special glasses. In this paper, we investigated the number of published manuscripts and patents and determined the correlation of research activities to the production of new PG materials. The United States, Japan and China have been leaders in photosensitive glass development and have contributed to an impressive rise of activity in PG based on a number of new publications, author keywords, affiliations and primary characterization techniques. We verified that the number of published fundamental PG studies was greater from academic institutions than from industrial laboratories. According to the European Patent Office, more than 6,228 patents have been globally filed prior to 2013 with the terms “photosensitive” and “glass” within the title or abstract. These numbers have continued to grow along with worldwide PG-related sales. Based on the Scopus database, for the same period, 1,301 PG documents (primarily manuscripts) were published with the same terms in the title, abstract or keyword list. Statistically, there have been fewer worldwide publications of manuscripts than patents.

Keywords: Glass, history, photosensitive, patent, technology.

1. INTRODUCTION

One decade after the first patents and manuscripts were published in the 1940s, a new type of commercially innovative material was introduced: the photosensitive glass (PG) [1]. It was discovered by the chemist and inventor Stanley Donald Stookey at Corning. PGs are in the field of material sciences and engineering and are based on the kinetics and crystallization mechanisms of vitreous materials, which are essential for the development of such special glasses. These materials have a number of special properties. PGs were originally categorized as a new photographic medium that made possible the permanent printing of 3D colored images within crystal-clear glasses [2]. According to Stookey, “photosensitive glass” [3] refers to “certain silicate glasses containing atomic species that are able of forming stable photographic images or figures into clear glass when subjected to light”. In fact, to reproduce a figure, a negative is positioned on a clear glass and briefly exposed to ultraviolet radiation from any of the several sources, including sunlight, sunlamps or other similar sources. After the negative is removed, the figure (or photograph) is fixed by increasing the temperature of the glass to approximately 600°C for a few minutes [1, 2]. The novelty of the procedure is in the mixing of transparent metallic nanocrystals (*e.g.*, gold, silver or copper) in trace quantities. On additional heat treatments, these nanocrystals act as crystallization seeds or nuclei for the growth of non-metallic crystals. Thus, the phenomena of crystallization occurs, confining an image or figure [1, 2]. Filed by Robert H. Dalton, a colleague of Stookey at Corning, in 1943 (studies started in 1937 [4]), the first patent considered the use of copper as a nucleating agent [5]. However, the term “photosensitive” was not used in this patent, and it was not feasible to produce images or display kinetics, as was later done by Stookey [3, 4]. In fact, Stookey’s patent was not published until almost seven years later on July 8th, 1950 [6]. Two patents were awarded to Stookey: *U.S.* Pat. N^{os}. 2,515,937 and 2,515,943; the first is shown in (Fig. **1**).

Photosensitive glasses and glass-ceramics have some characteristics in common: they are transparent, strong and tough, chemically durable, and have zero or low porosity. These materials have been used in a wide array of applications,

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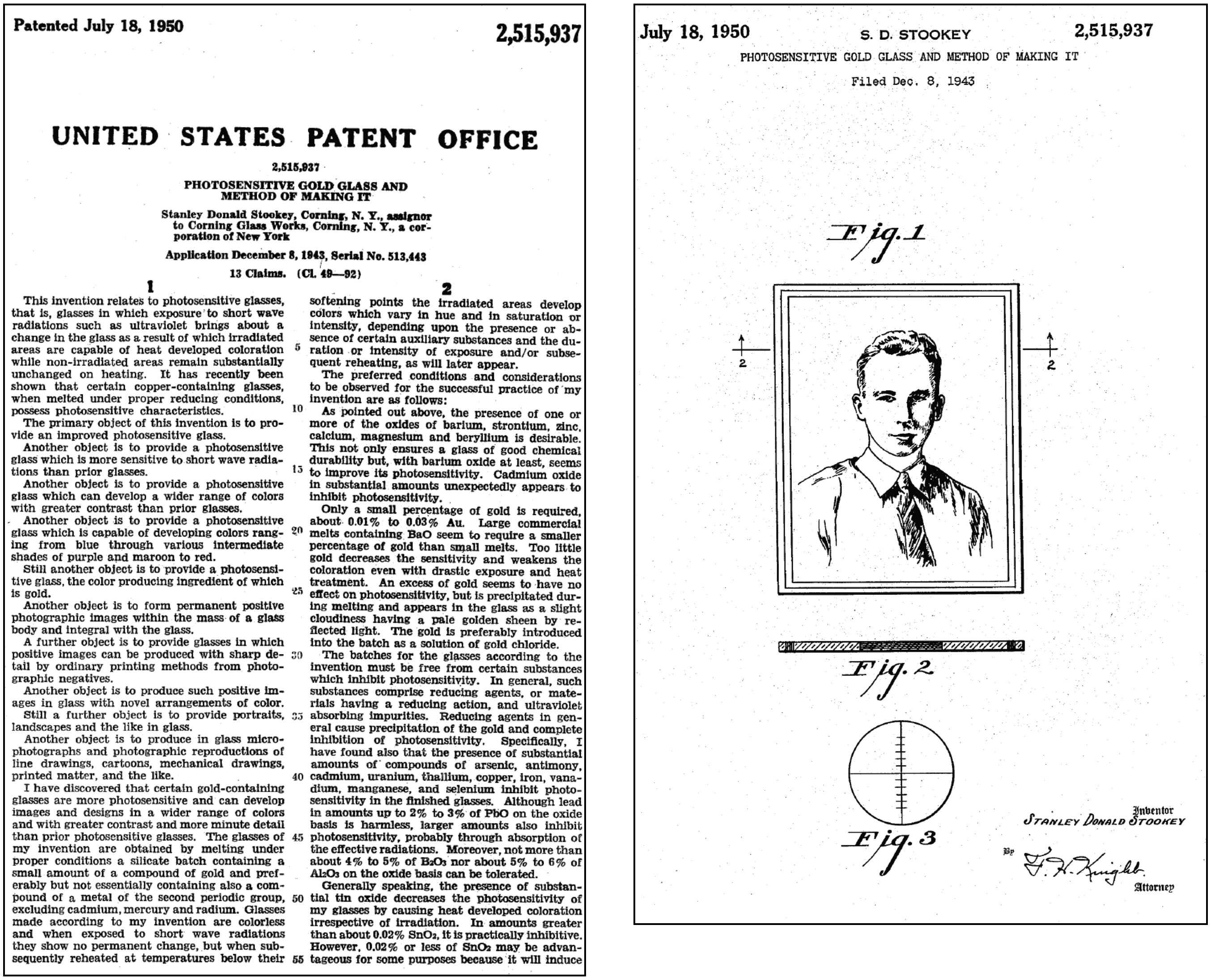

Patented July 18, 1950 **2,515,937**

UNITED STATES PATENT OFFICE

2,515,937

PHOTOSENSITIVE GOLD GLASS AND METHOD OF MAKING IT

Stanley Donald Stookey, Corning, N. Y., assignor to Corning Glass Works, Corning, N. Y., a corporation of New York

Application December 8, 1943, Serial No. 513,443

13 Claims. (Cl. 49—92)

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This invention relates to photosensitive glasses, that is, glasses in which exposure to short wave radiations such as ultraviolet brings about a change in the glass as a result of which irradiated areas are capable of heat developed coloration while non-irradiated areas remain substantially unchanged on heating. It has recently been shown that certain copper-containing glasses, when melted under proper reducing conditions, possess photosensitive characteristics.

The primary object of this invention is to provide an improved photosensitive glass.

Another object is to provide a photosensitive glass which is more sensitive to short wave radiations than prior glasses.

Another object is to provide a photosensitive glass which can develop a wider range of colors with greater contrast than prior glasses.

Another object is to provide a photosensitive glass which is capable of developing colors ranging from blue through various intermediate shades of purple and maroon to red.

Still another object is to provide a photosensitive glass, the color producing ingredient of which is gold.

Another object is to form permanent positive photographic images within the mass of a glass body and integral with the glass.

A further object is to provide glasses in which positive images can be produced with sharp detail by ordinary printing methods from photographic negatives.

Another object is to produce such positive images in glass with novel arrangements of color.

Still a further object is to provide portraits, landscapes and the like in glass.

Another object is to produce in glass microphotographs and photographic reproductions of line drawings, cartoons, mechanical drawings, printed matter, and the like.

I have discovered that certain gold-containing glasses are more photosensitive and can develop images and designs in a wider range of colors and with greater contrast and more minute detail than prior photosensitive glasses. The glasses of my invention are obtained by melting under proper conditions a silicate batch containing a small amount of a compound of gold and preferably but not essentially containing also a compound of a metal of the second periodic group, excluding cadmium, mercury and radium. Glasses made according to my invention are colorless and when exposed to short wave radiations they show no permanent change, but when subsequently reheated at temperatures below their

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softening points the irradiated areas develop colors which vary in hue and in saturation or intensity, depending upon the presence or absence of certain auxiliary substances and the duration or intensity of exposure and/or subsequent reheating, as will later appear.

The preferred conditions and considerations to be observed for the successful practice of my invention are as follows:

As pointed out above, the presence of one or more of the oxides of barium, strontium, zinc, calcium, magnesium and beryllium is desirable. This not only ensures a glass of good chemical durability but, with barium oxide at least, seems to improve its photosensitivity. Cadmium oxide in substantial amounts unexpectedly appears to inhibit photosensitivity.

Only a small percentage of gold is required, about 0.01% to 0.03% Au. Large commercial melts containing BaO seem to require a smaller percentage of gold than small melts. Too little gold decreases the sensitivity and weakens the coloration even with drastic exposure and heat treatment. An excess of gold seems to have no effect on photosensitivity, but is precipitated during melting and appears in the glass as a slight cloudiness having a pale golden sheen by reflected light. The gold is preferably introduced into the batch as a solution of gold chloride.

The batches for the glasses according to the invention must be free from certain substances which inhibit photosensitivity. In general, such substances comprise reducing agents, or materials having a reducing action, and ultraviolet absorbing impurities. Reducing agents in general cause precipitation of the gold and complete inhibition of photosensitivity. Specifically, I have found also that the presence of substantial amounts of compounds of arsenic, antimony, cadmium, uranium, thallium, copper, iron, vanadium, manganese, and selenium inhibit photosensitivity in the finished glasses. Although lead in amounts up to 2% to 3% of PbO on the oxide basis is harmless, larger amounts also inhibit photosensitivity, probably through absorption of the effective radiations. Moreover, not more than about 4% to 5% of B_2O_3 nor about 5% to 6% of Al_2O_3 on the oxide basis can be tolerated.

Generally speaking, the presence of substantial tin oxide decreases the photosensitivity of my glasses by causing heat developed coloration irrespective of irradiation. In amounts greater than about 0.02% SnO_2, it is practically inhibitive. However, 0.02% or less of SnO_2 may be advantageous for some purposes because it will induce

Fig. (1). *Left*: the first page of *United States* photosensitive glass patent *U.S.* 2,515,937 applied on December 8th, 1943, [6] and published on July 8th, 1950. *Right*: an image application of the photosensitive process; there is a bluish portrait of the author as the first figure in the patent. At that time he used gold particles with a basic glass, with heat treatments between 500 to 600°C over a few minutes. See www.uspto.gov.

ranging from portraits and figures, photographic murals, 3D images, decorative windows, displays, ornamental tiles, and many engineering applications, including military uses.

Glassmaking is an old technology that dates back approximately 5 millennia. Glass is one of the most relevant, useful and effective materials throughout human history. The process of glassmaking consists of melting raw materials, such as sand, alkali carbonates and lime, at approximately 1400°C. This has been a common technique throughout recorded history due to its simplicity, adaptability and potential applications in a number of fields. Glassmaking can also be modified for mass production. As noted by Zanotto [7], the thermodynamics and kinetics of nucleation and crystal growth are key scientific problems that control the glass-forming ability of molten liquids and the terminal stability of glass against devitrification. The basics behind the nature and rules of glass crystallization involve the mechanisms, thermodynamics and kinetics of crystal nucleation, growth and overall surface crystallization.

Initially, the manufacture of glass-ceramics was empirical and based on experimentation. The history of glass-ceramic production dates back a century to 1898 when Gustav Tammann [8] published the first modern scientific paper on glassmaking, which described the behavior of glass-ceramics production by controlling the nucleation I and growth U processes. He studied the crystallization of organic liquids and suggested the following method, which is now known as the Tammann, or "development" approach [9]. Crystals nucleated in a glass matrix at a low temperature, T_n, are developed to sizes sufficient for microscopic observations at a higher temperature, $T_d > T_n$. The development temperature T_d is determined based on rules for the nucleation (I) and growth (U) rates: the nucleation rate at T_d [$I(T_d)$] should be lower than the nucleation rate at T_n [$I(T_n)$], and the growth rate at T_d [$U(T_d)$] should be greater than the growth rate at T_n [$U(T_n)$]. In the last half century, this process has gained widespread popularity in academia as a method for the manufacture of homogeneous glassy materials. Stookey empirically determined the characteristic temperature T_d of photosensitive glasses.

Recently, Glebov [10] proposed a kinetics model of a photoinduced process based on a new photosensitive composition for 3D hologram production, photo-thermo-refractive glass (PTRG). PTRG is a multicomponent silicate glass composition with cerium, silver and fluorine as the primary dopants, which shows a decreasing refractive index after exposure to UV light and thermal heat treatment. In this material, a sequence of photochemical and photo-physical reactions occurs as follows: *i*) a UV incident light photoionizes trivalent cerium; *ii*) a released electron is captured by an Ag^+ ion, which is converted to Ag^0; *iii*) a thermal heat treatment of UV-exposed glass mobilizes silver atoms and creates silver nanocrystals, which promote the formation of nucleation centers that control the precipitation of the NaF crystalline phase; *iv*) additional interactions between sodium fluoride nanocrystals and the glass matrix at elevated temperatures causes a modification of the refractive index; and *v*) a difference between the crystallization rates in exposed and unexposed areas develops a photo-controlled refractive index modulation.

2. STANLEY DONALD STOOKEY AND A BRIEF HISTORY OF COMMERCIAL PHOTOSENSITIVE GLASS

Dr. Stanley D. Stookey (1915-2014) was an American scientist and inventor. According to the European Patent Office (EPO), Stookey was awarded 116 patents covering glassy and glass-ceramic materials subject matter. His discoveries and inventions have considerably affected the development of new ceramic compositions, such as eyeglasses, sunglasses, cookware, military systems and electronics. At Corning, he was a research director for nearly five decades and promoted research and development in glasses and ceramics.

Stookey attended Coe College from 1934 to 1936 and obtained his first *Magna Cum Laude* degree in chemistry and mathematics. After graduation Stookey then went to Lafayette College in Easton, Pennsylvania in 1937. In 1938, he received his MsC in chemistry from Lafayette College. Stookey then went to Massachusetts Institute of Technology in Cambridge where he earned a PhD in chemistry in 1940. He was offered a job at Corning Glass Works in the same year, despite knowing little about glass. It was in this way that he carried out studies on glass-ceramics, which led him to several patents. His multimillion dollar products include Fotoform, Cercor, Pyroceram, opal glass, photosensitive glass, a heat resistant glass used in missile nose cones, photochromic glass, and ophthalmic glass eyewear that darken and fade according to environmental conditions. These particular glass lenses were first made available to consumers by Corning Glass Works in the 1960s as sunglasses [11].

In particular, while working for Corning, Stookey developed another remarkable glass product that would forever change cooking. This glass is known as CorningWare. This glass is used in dishes that can be used to both bake a casserole and freeze the leftovers. CorningWare is also used for making all sorts of dishware and for making stove tops meals. According to Stookey, it was a lucky accident that launched glass-ceramics [12,13]. Stookey once said, "I am most proud of opening up a whole new field of science – the nucleation of crystallization of glass – that produced all types of new crystalline products with so many different useful properties." [11]. In 1987, Stookey retired from Corning Glass Works.

Our objective is to present an overview of the historical tendencies and current status of PG studies. We hope this paper can be used during discussions about future guidelines for photosensitive glass studies by describing the development of PGs based on the literature.

3. METHODOLOGY

In this work, we considered the number of published manuscripts catalogued in the "Life Sciences" (which comprises 4,300 journal titles), "Health Sciences" (6,800 titles), "Physical Sciences" (7,200 titles) and "Social Sciences & Humanities" (5,300 titles) libraries of the Scopus bibliographic database from Elsevier due to wide application range of PGs. We searched for papers with the words "photosensitive" and "glass" in the *title*, *abstract* or *keywords* of the article. Based on this specific search procedure, we excluded many other photosensitive-related articles. However, this approach provided a broader dataset and consequently, sufficient data for statistical analyses.

The total number of photosensitive glass-related publications registered at Scopus was 1,301 based on the keywords "*photosensitive*" and "*glass*" appearing in the article title, keyword list or *abstract*, for all document types, including letters, conference proceedings, *errata* and technical notes between 1940 and 2013. To further simplify our dataset, we restricted the search to journal articles. Our search returned 819 photosensitive glass-related manuscripts from the Scopus database. A similar search carried out on the Web of Science (Thomson Reuters Scientific) returned 1,226 papers when searching for the terms "*photosensitive*" and "*glass*" in the title and topic keywords. The articles obtained through this approach were grouped according to the research field, publication date, journal title, country of origin, affiliation, and type of glass studied.

We also executed a similar search of the patent literature using the European Patent Office database. This search considered patents awarded between 1940 and 2013 with the keywords in the title or abstract as was performed in the Scopus search. The search returned approximately 6,228 PG patents issued worldwide. These patents were sorted according to issue date and inventor.

4. RESULTS & DISCUSSION

Fig. (**2**) shows the number of photosensitive glass-related documents published and granted by decade, as found through the Scopus database. Here we considered the following search strategies: the PG keywords were found in the article title, abstract or keywords list (1,301 documents); only in the abstract (925 documents) or only in the title (592 documents).

Fig. (**2**) also shows that the number of publications on PG research works exponentially increased in recent years, which correlated with the observations made by Mauro and

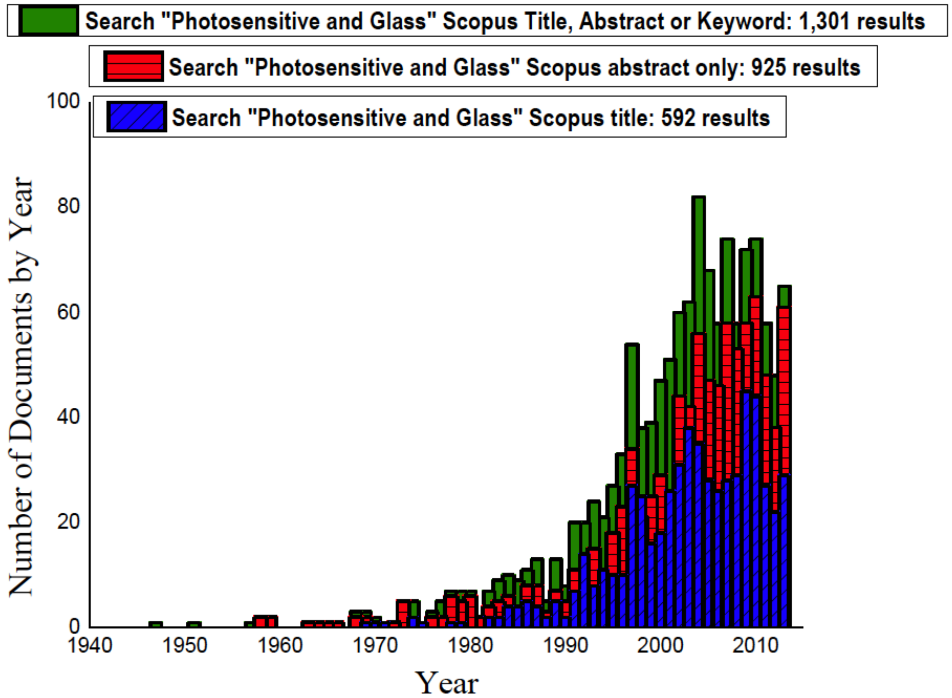

Fig. (2). Publications of "Photosensitive glass" documents: considering the keyword in the article title, abstract or keyword (1,301 document results); only abstract (925 document results) and only title (592 document results). Data from www.scopus.com.

Zanotto [14]. Regarding photosensitive glass, the first manuscript was published anonymously in 1947 [2], in the "The Chemical News Parade" column of the *Chemical Engineering News* magazine. Of these PG documents, 62.90 % were Articles, 30.88 % were Conference Papers and only 1.08 % were Reviews. Other reported categories included Book Chapters, Conference Reviews, Reports and Letters.

According to (Fig. **3**), the most prolific institution in terms of publications on photosensitive glass was the University of Central Florida (UCF) in USA, by Prof. Leonid Glebov. Asian universities, including RIKEN (the Institute of Physical and Chemical Research) and the Tokyo Institute of Technology (both from Japan), Nanyang Technological University (Singapore), and the University of Southampton (UK), were also part of the top five institutions in a list of 160 institutions. The most prolific authors were Profs. Koji Sugioka and Katsumi Midorikawa, both from RIKEN, followed by Leonid Glebov, from UCF.

If we consider the breakdown of photosensitive glass-related publications by country (see Fig. **4**), the United States aggregated the highest number of overall publications, followed by Japan and China (South Korea, Germany, Russian Federation, France and the United Kingdom were also ranked). According to Mauro and Zanotto [14], these three countries were leaders in glass research, followed by Russia and three European countries. Outside of Europe, Canada and India were also highly ranked.

Fig. (**4**) also presents a geographical analysis of active researchers in the PG field. The United States had the highest percentage at 16.05 % of 67 countries, followed by Japan (13.52 %), China (7.30 %), South Korea (6.00 %) and Germany (6.00 %). The higher percentage of Asian researchers (taking into account only the top five institutions) was likely due to greater contributions of government allocated funds for PG research. Please note that Brazil and the Ukraine were 20th on the list with 13 patents each.

According to Mauro and Zanotto [14], there has been an increasing rate of glass research from Chinese institutions in the past few decades, surpassing those of every other country. Other countries that presented notable increases in research activity were India and South Korea. Since the mid-nineties, both rates have grown rapidly, while the growth rates in research activity has diminished or even become negative in all other countries. The abrupt increase in Chinese research is correlated with a noticeable slowing of the general glass research growth rate in the United States [10]. While this deceleration was troubling, the fall in research rates was more dramatic in many of the other traditionally strong countries, such as United Kingdom, Italy, and France, all of which actually produced fewer research publications in last two decades. According to these data, as presented in (Fig. **4**), North America and Asia have become prominent centers for the development of new technologies for photosensitive glass products.

According to Zanotto [15], while much is already known about glass-ceramics technology, many challenges in the development of photosensitive glasses and glass-ceramics remain. These include new, alternative compositions, more potent nucleating agents, and new or improved crystallization processes.

Additionally, profound understandings of the control processes that govern photothermal-induced nucleation with

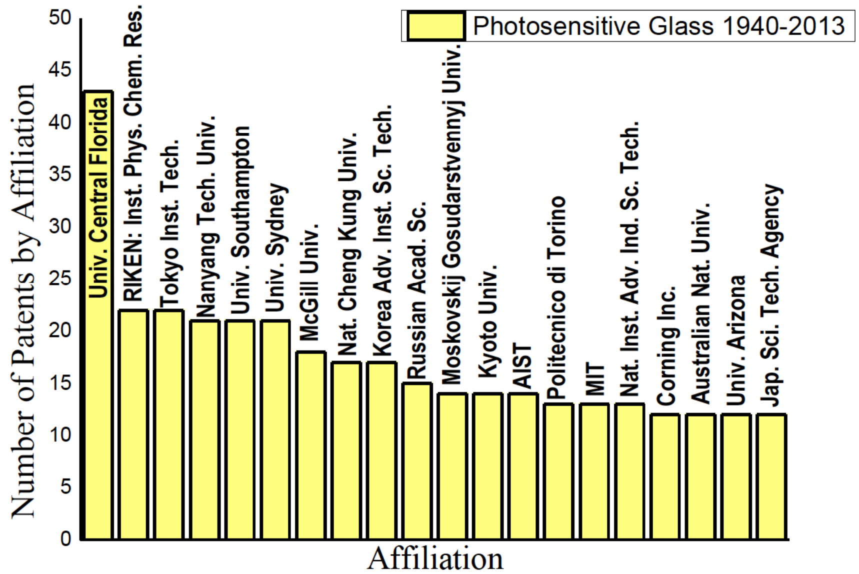

Fig. (3). Total number of publications on photosensitive glass (1940-2013), sorted by affiliation (top 20). University of Central Florida of the United States leads this ranking, followed by RIKEN: the Institute of Physical and Chemical Research of Japan. Overall, there was a mix of Asian, European, and American institutions. It is relevant to stress the presence of Corning, Inc., within the 20 most prolific institutions in these rankings. Data from www.scopus.com.

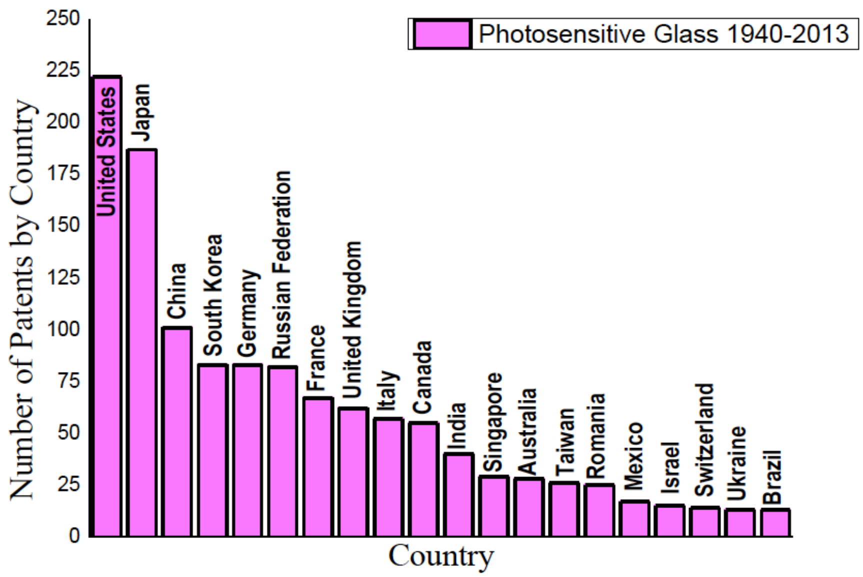

Fig. (4). Most prolific 20 countries in the history of photosensitive glass research (1940-2013). The United States, Japan and China are the leaders overall in photosensitive glasses. Data from www.scopus.com.

or without chemical etching and the development of harder, stiffer, stronger and tougher special glasses with increased transparency are also timely. These glasses have a wide range of potential properties due to their variety of compositions, thermal treatment protocols and resulting microstructures. These, combined with the flexibility of high-speed hot-glass fabrication techniques will ensure the continued growth of glass technology [15].

The most prominent journals within the PG community include *Proceedings of SPIE*, from the International Society for Optical Engineering (19.38 %), *Journal of Non Crystalline Solids* (5.39 %), *Optics Letters* (2.87 %), *Applied Physics Letters* (2.52 %) and *Optics Express* (2.41 %). Additionally, there were a number of applications and sources of publications, in total, 872 manuscripts. The first journal published approximately four times the number of photosensitive glass-related articles compared with the second most popular journal, as shown in (Fig. **5**).

PG-related publications were also categorized by broad scientific field, such as *Physics and Astronomy* (28.23 %),

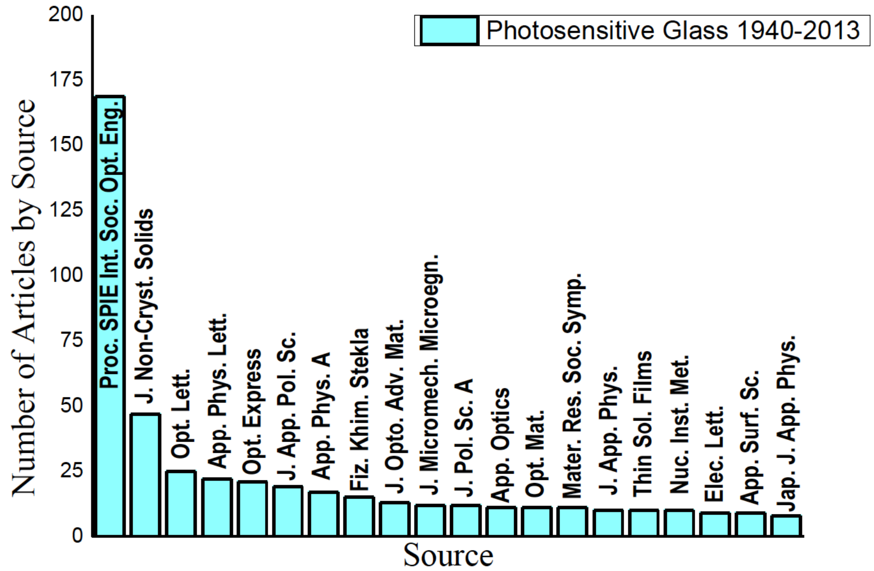

Fig. (5). Cumulative number of photosensitive glass-related publications by journal from 1940 to 2013. *Proceedings SPIE* leads this journal ranking by a wide margin. It is interesting to note that several physics/optical journals follow in the ranking. Data were collected from 143 sources worldwide in the period analyzed from www.scopus.com.

Materials Science (24.87 %), *Engineering* (24.51 %), *Chemistry* (6.73 %) *Computer Science* (4.13 %), *Mathematics* (2.74 %) and *Chemical Engineering* (2.42 %). These publications corresponded with publications in relevant specialized journals.

Over 6,228 PG patents from the European Patent Office (EPO) were granted between 1940 and 2013 (Fig. **6**). This result suggested that a number of innovative studies toward new photosensitive glasses addressed industrial challenges and that the applications for PG were expanding. There was a noted decrease in the number of PG patents since 1980, as shown in Fig. **6**. This behavior was also observed by Mazurin and Priven [16] when they analyzed the number of glass patents and publications for different year ranges: *i*) a lethargic growth rate (up to 1960 for patents and 1950 for scientific publications), with significant decreases during the Second World War; *ii*) an enthusiastic growth rate between 1960 to 1973; and *iii*) random fluctuations with an overall gradual positive growth rate after 1973 coinciding with the global oil crisis. A common industrial practice was and is to register several related patent applications in different countries for the same invention. Therefore, the number of patents issued globally was greater than the number of unique inventions disclosed. This is seen in other technologies, including glassy X-ray tube patents [17] and even the industrial float glass process [18].

Governments have an important role in improving, supporting and providing directions in innovation and producing potential commercial patents. Government agencies, such as the National Science Foundation (*U.S.*), the Japan Science and Technology Agency (JST), the National Natural Science Foundation of China (NSFC), the European Union, the Deutsche Forschungsgemeinschaft of Germany (DFG), the Engineering and Physical Sciences Research Council (EPSRC) of the UK, and CAPES, CNPq and FAPESP in Brazil are examples of programs that have supported scientists, institutes, industries and companies in the development of energy efficient, green-technological solutions. PG technologies have considerable promises. Additionally, new and performance-enhancing materials have been prepared as a result from the steadily growing research communities and funding support.

A search in the EPO for the aforementioned keywords in the title and abstract fields indicated that the most prolific companies in PG research were: NEC Corp. (63 patents), Corning, Inc. (60), IBM (26), Nippon Sheet Glass Co. (14), Saint Gobain (9), Schott (7), Toyota (2) and Aerospace Corp. (1). The overall PG portfolio is considered a promising research focus due to their number of applications in industry. Thus, a large number of potential publications, patents, products and processes are expected in the near future. In particular, new improvements in the applicability of these special glasses and various new innovations are waiting to be discovered [2, 15, 16].

However, the limited number of published manuscripts have yet to reveal many important issues relevant to photosensitive glasses. More experiments, modeling and simulation studies on the fundamental properties of these materials show great promise in a number of applications. Nevertheless, a complete understanding of PG structure and properties is lacking. An increasing interest in published patents does show an increasing interest in the field.

5. CONCLUSIONS OR FINAL COMMENTS

Glass is a transparent solid with good chemical durability that breaks easily. They are among one of the most ancient materials in human history; however, our knowledge of their structure is far from complete. Upon closer inspection, photosensitive glasses constitute an intriguing class of materials

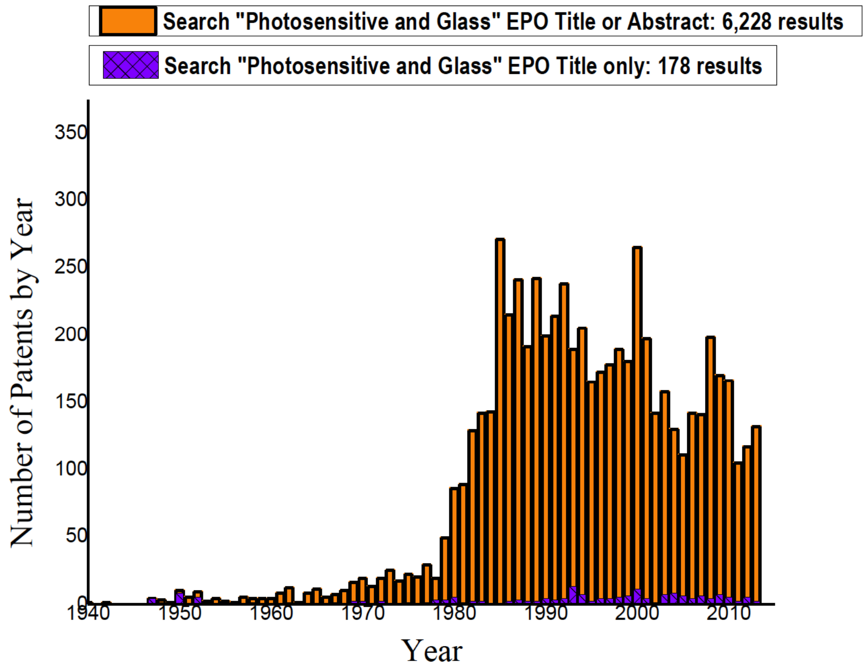

Fig. (6). Frequency distribution results for patent search using "Photosensitive" and "Glass" in the *title* only or *title or abstract*. Data considering results between 1940 and 2013 from www.epo.org.

from the perspectives of basic science and industrial applicability.

In this work, we presented the advances in PG research since the 1940s. We also discussed one of the most widely used methods for manufacturing PG and how this method ensured high excellence and high productivity for many industrial sectors. According to the European Patent Office, more than 6,228 patents have been filed worldwide in these 73 years that have used the terms "*photosensitive*" and "*glass*" in the title or abstract. According to the Scopus database, for the same period, 1,301 PG documents were published and most were manuscripts.

Patents could be considered indicators of successful innovations. The number of photosensitive and glass-ceramics patents have been increasing due to: *i*) the potential impact of such special glasses; *ii*) their rapid synthesis; and *iii*) their recognized relevance in industries. However, many patents to the same, unique invention have been filed in multiple patent offices worldwide.

The publication rate has roughly increased exponentially since the end of World War II. Overall, the most significant countries for photosensitive and glass-ceramics studies are the *U.S.*, Japan and China, which indicate high levels of advanced research and development activities.

The demand for photosensitive glass processes can be achieved are being addressed by the approximately 150 universities and research institutes around the world. More recently, the University of Central Florida (USA) and RIKEN have become the primary centers for PG research.

The number of globally issued PG patents remains lower than the number of published scientific manuscripts. This result indicated the very high level of initial activity on technological research for photosensitive glasses. Thus, many challenges exist in the photosensitive glasses process, and a number of fundamental questions remain open. Currently, it is still necessary to have a better understanding of the processes that control nucleation and crystal growth in countless glass materials. In the field of glass science, studies are still being conducted to describe kinetic processes from theoretical models. In the field of glass technology, the literature reports new and improved photosensitive glasses, most of which have reached commercial production. Other than Corning, Inc., no other industrial research lab is on the top 20 list of institutions conducting PG studies. The *U.S.* maintains a significant fraction of the filed photosensitive patents. In particular, the first application of photosensitive glass was made in USA by S. D. Stookey. The glass industry and the world will continue to benefit from his glass studies and inventions for years to come.

CONFLICT OF INTEREST

The author confirms that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

The authors wish to thank Brazilian CNPq agency for financial support from grant numbers 305373/2009-9, 479799/2010-5, 300938/2012-8 and 471546/2012-7.

REFERENCES

[1] Anonymous. "Products and Processes". *Chem. Eng. News* 25 (1947) 1822-1823

[2] Anonymous. "Photosensitive Glass Developed". *Chem. Eng. News* 25 (1947) 3504-3505.

[3] S. D. Stookey. "Chemical Machining of Photosensitive Glass". *Ind. Eng. Chem*. 45 (1953) 115-118.

[4] S. D. Stookey. "Photosensitive Glass: A New Photographic Medium". *Ind. Eng. Chem*. 41 (1949) 856-861.

[5] R. H. Dalton. "Glass Article and Method of Making It". *U. S.* Patent 2,326,012 (1943).

[6] S. D. Stookey. Photosensitive Gold Glass and Method to Make It. *US Patent* 2,515,937 (1950).

[7] E. D. Zanotto. "Glass Crystallization Research - A 36-Year Retrospective. Part I, Fundamental Studies". *Int. J. App. Glass Sci.* 4 (2014) 1-15.

[8] G. Tammann. "Uber die Abhangigkeit der Zahl der Kerne". *Z. Phys. Chem*. 25 (1898) 441-479.

[9] V. M. Fokin, E. D. Zanotto, N. S. Yuritsyn, J. W.P. Schmelzer. "Homogeneous crystal nucleation in silicate glasses: A 40 years perspective". *J. Non-Cryst. Solids* 352 (2006) 2681-2714.

[10] L. B. Glebov. "Kinetics modeling in photosensitive glass". *Opt. Mat.* 25 (2004) 413-418.

[11] Kathy L. Woodard. "Profiles in Ceramics: S. Donald Stookey". The American Ceramic Society Bulletin (March 2000), 34-39.

[12] Stookey, S. Donald, "Journey to the Center of the Crystal Ball: An Autobiography'', American Ceramic Society (1985), ISBN 0-916094-69-3.

[13] Stookey, S. Donald, "Explorations in Glass: An Autobiography'', John Wiley & Sons (2006), ISBN 978-1-57498-124-7.

[14] J. C. Mauro, E. D. Zanotto. "Two Centuries of Glass Research: Historical Trends, Current Status, and Grand Challenges for the Future". *Int. J. App. Glass Sci.* 5 (2014) 1-15.

[15] E. D. Zanotto. "A bright future for glass-ceramics". *Am. Ceram. Soc. Bull*. 89 (2010) 19-27.

[16] A. I. Priven, O. V. Mazurin. "Patenting the Glass Compositions During the Last Century". *Recent Patents Mat. Sci.* 1 (2008) 12-20.

[17] M. L. F. Nascimento. Brief History of X-Ray Tube Patents. *World Patent Info*. 37 (2014) 48-53.

[18] M. L. F. Nascimento. Brief History of the Flat Glass Patent Sixty Years of the Float Process. *World Patent Info*. 38 (2014), 56-60.