July 18, 1950 S. D. STOOKEY 2,515,937

PHOTOSENSITIVE GOLD GLASS AND METHOD OF MAKING IT

Filed Dec. 8, 1943

Fig. 1

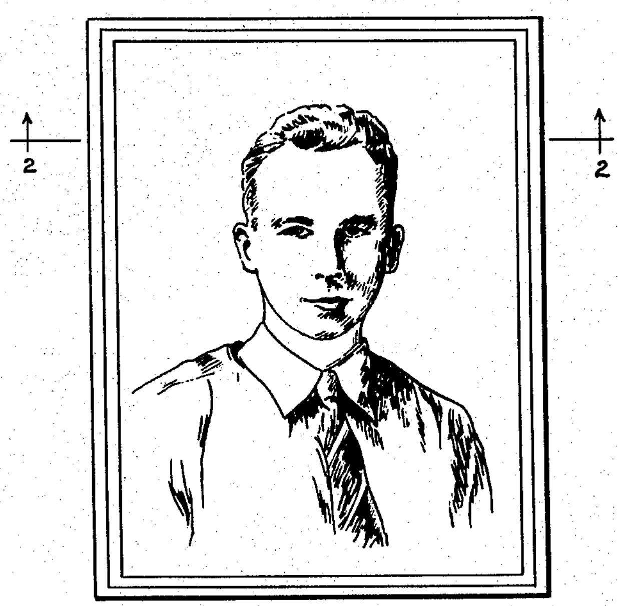

Fig. 2

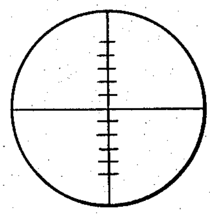

Fig. 3

Inventor
STANLEY DONALD STOOKEY

By F. H. Knight
Attorney

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)

1

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

2

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 in the unexposed areas a heat developed coloration which is different from that of the exposed areas.

The addition of oxidizing agents to the new glasses does not increase the rate of photosensitive reaction of the resulting glasses, but intensifies the colors obtained by exposing and reheating the glass.

The presence of a very small percentage of cerium in my glasses has several important effects and advantages despite the fact that cerium in substantial amounts may absorb the effective radiations. It greatly improves the sensitivity of the glasses, i. e., it increases the exposure speed ten-fold or decreases the time of exposure by a factor of ten. In a glass which has been oxidized by the use of an oxidizing agent, such as nitre ($NaNO_3$), or saltpeter (KNO_3), cerium increases the color intensity which may be produced by a given quantity of gold on irradiation and heat treatment. As a further advantage of the presence of cerium in the glass, the range of colors which can be developed is extended. Amounts as small as about 0.05% CeO_2 are sufficient to produce such effects. Amounts in excess of 0.05% cause absorption of the effective radiations and decrease or inhibit photosensitivity.

The colors obtainable by irradiating and heating my glasses will vary with the exposure and the heat treatment and will range from blue through various intermediate shades of lavender, purple and maroon to a deep red. The coloration passes progressively through this range of colors in the recited order as time or intensity of exposure is increased. Using a constant heat treatment, the coloration of a heated irradiated glass begins at the irradiated surface and advances progressively into the glass as the time or intensity of exposure is increased. Blue is usually the first color to appear and after it has passed into the glass it is followed by a red coloration, the combination of the two colors causing the glass to appear lavender, purple or maroon. With sufficiently long heating the blue color ultimately is entirely replaced by red. Likewise, with an exposure which is insufficient to affect the glass throughout, the heat-developed color will also change through the above described range as the time or temperature of heat treatment is increased. With very long exposures, the glass may be so affected that only a red color can be developed by heat treatment.

The presence of about 0.02% or less of SnO_2 activates the glass sufficiently to cause the ultimate development of color in the unexposed areas during heating after the exposed areas have already become colored. The earlier developed coloration of the exposed areas progressively changes in hue as heating is continued so that it always differs from the color developed later in the unexposed areas, thus providing in a single

treatment a two-tone design or an image with or background of contrasting color.

The time of exposure necessary to obtain an effect in my glasses which can be developed into a coloration by heating will vary, depending upon the composition of the glass, the color effects desired and the intensity of the effective radiations, i. e., the type and distance of the source of the radiations from the glass during exposure. A five minute direct exposure at eight inches from a carbon arc will generally suffice for the production of a blue color in a glass containing gold and cerium when subsequently heated. If different areas of a body composed of my glass are exposed for different lengths of time or with different intensities and the body is then uniformly reheated, the glass will become colored and the colors produced in the exposed areas will differ from one another and may vary from blue to red, depending upon the times and intensities of the exposures. For example, a blue portrait may be produced on a colorless background surrounded by a red border, as will later be shown.

Although ultraviolet emitting lamps, such as the carbon arc or the quartz mercury arc, are convenient sources of radiations effective for my purpose, it is my intention that treatment with X-rays, radioactive radiations, etc., shall be included in the scope of the present invention.

The temperature and time of heat treatment will depend upon how greatly the gold in the glass has been affected by irradiation. The most suitable temperatures are between 500° C and 600° C. Long treatments at the lower temperatures are as effective as short treatments at the higher temperatures. Very drastic heat treatments near the softening temperature of the glass may cause the development of some coloration in unexposed areas. Normally, however, the glass may be reheated repeatedly for thirty minute intervals at 550° C. without coloration of unexposed areas. Such areas, if subsequently exposed, will thereafter become colored on being heated. Exposed areas which are repeatedly reheated undergo color changes as above pointed out and progress from blue through intermediate shades to red. Thus, also, according to the invention, differentially colored designs and photographic images may be produced in a glass body by exposing only previously unexposed areas one after another, using the same exposure time and intensity and reheating the glass after each exposure.

As examples illustrating glass compositions suitable for use according to my invention, the following batches, in parts by weight, are given:

Table I

	1	2	3	4	5	6	7	8
SiO_2	100	100	100	100	100	100	100	100
Na_2CO_3	42	41	42	37	42	48	45	40
$Al(OH)_3$	3.3	3.3	3.3	3.3	3.3	6	4	
$BaCO_3$	15	15	15	15	15			
H_3BO_3							5	
Gold	.021	.014	.013	.014	.013	.018	.018	.018
CeO_2			.052	.052				
$NaNO_3$		6		6		3.7	3.7	3.5
Cryolite				10				
SnO_2					.029			

Compositions 1 to 5 inclusive are examples of batches for glasses which contain a second group oxide, specifically BaO. Compositions 6 to 8 inclusive are similar examples which contain no second group oxide. It will be observed that the batches all contain gold equivalent to about 0.01% of the finished glass. Batches Nos. 2, 4, 6, 7, and 8 contain in addition nitre; No. 3 contains CeO_2 equivalent to about 0.04% of the glass, but no nitre; No. 4 contains both CeO_2 and nitre; and No. 5 contains tin oxide equivalent to about 0.02% of the glass.

It will further be noted that composition 4 also contains a small quantity of cryolite. This material functions as a fining agent. As hereinbefore pointed out, arsenic and antimony, the usual fining agents, cannot be used in my glasses. I have found that fluorine acts as a fining agent in these glasses and that any fluorine compound which contains no inhibitory substance can be used, such as cryolite, fluorspar, sodium silicofluoride, sodium fluoride, etc.

The glasses of the above compositions are colorless, highly photosensitive, and can develop a variety of colors and combinations of colors subject to the necessary conditions of time and/or intensity of exposure or heat treatment, as hereinbefore explained. The substitution of beryllium, magnesium, calcium, zinc, or strontium for barium in substantially the same quantities in the above compositions will produce glasses having substantially the same characteristics.

To illustrate the improved sensitivity and color range of my new glases as compared with prior glasses, the following table shows the exposure time and heat-developed color obtained with a number of glasses comprising glasses resulting from melting batches 2, 3, and 4, and the prior copper-containing photosensitive glass. Small plates of these glasses were simultaneously exposed for 1, 2, 4, 8, 16, and 32 minutes, respectively, at a distance of eight inches from a carbon arc. The exposed plates, together with one unexposed plate of each glass, were heated simultaneously for thirty minutes at about 550° C.

For a better understanding of the remarkable capabilities of the invention for the production of permanent photographic images within a glass body, reference is had to the accompanying drawing in which

Fig. 1 represents a glass plate having a thickness of about 1/8 inch, a length of about 4 1/2 inches and a width of about 3 1/2 inches, and bearing within its mass a centrally located portrait of one color and a narrow circumscribed stripe of another color, but being otherwise colorless;

Fig. 2 is a sectional view on the line 2—2 of Fig. 1; and

Fig. 3 is a reticle for an optical instrument comprising a small, transparent, homogeneous glass disc having a plurality of extremely thin planes of color extending perpendicularly inward from one face of the disc and forming a cross hair when viewed from either face of the disc.

The decorated plate shown in Fig. 1 was prepared as follows:

A colorless, transparent and polished plate of the stated size composed of glass composition 4 of Table I was covered with a light-proof mask which permitted exposure of only that area which was to be provided with the circumscribed border stripe. The plate was thereafter exposed for about 15 hours at a distance of about twenty inches from a quartz mercury arc lamp. The mask was then removed and an ordinary photographic negative of the desired portrait was superimposed over the central portion of the plate and the area surrounding the portrait was again masked. The whole was exposed at about eight inches from a carbon arc, the negative being between the arc and the sensitive glass plate. After about 37 minutes exposure the plate was removed, the negative and mask were separated therefrom and the exposed plate was slowly heated uniformly to about 550° C. After about

Table II

Exposure Time Minutes	Heat Developed Color			
	Glass #2	Glass #3	Glass #4	Prior Copper Glass
0	Colorless	Colorless	Colorless	Colorless.
1	Barely detectable blue	Pale lavender	Very faint blue	Do.
2	Very faint blue	Lavender	Pale blue	Do.
4	Very pale blue	Dark lavender	Dark blue	Do.
8	Pale blue	Orange red	Purple	Barely detectable pink.
16	Light blue	do	Dark purple	Dark pink.
32	Dark blue		Maroon	Do.

As a result of the unusual photosensitivity of my new glasses, photographic negatives can be employed, in the conventional manner, using an ultraviolet lamp or other source of short wave radiations to make positive images in the glass which are equal in detail and contrast to positive images printed in like manner upon photographic printing paper. However, the glass plates and cellulosic films, which are used as supports for the emulsion of ordinary photographic negatives have a substantial absorption for ultraviolet. Although such absorption is not sufficient to prevent printing in my glasses with ultraviolet in the ordinary manner, I have found that it practically quadruples the exposure time necessary to produce a given effect. This difficulty can be avoided by using negatives in which the emulsion is supported on plates of ultraviolet transmitting glass, or by forming the emulsion directly upon the glass in which the positive image is to be developed.

30 minutes at this temperature the plate was slowly cooled. As a result of the above described treatment the plate thereafter bore within its mass a permanent positive image which was a faithful reproduction of the negative and which was surrounded by a bordering stripe of contrasting color. As shown in Fig. 2, the color of the portrait was blue and the color of the border stripe was red. The colors could have been reversed by reversing the exposure times and intensities. Other color combinations could also have been produced by varying the different factors as hereinbefore explained.

The reticle of Fig. 3 may conveniently be made by preparing an enlarged drawing of the desired cross hairs, photographing the drawing to form a negative thereof on a greatly reduced scale and then employing the negative to transfer a positive photographic image to the glass disc in the manner employed for making the portrait shown in Fig. 1.

In a similar manner mechanical drawings, cartoons and various sorts of sketches, etchings, paintings and the like can be photographed, printed and developed in the glasses of my invention. By reducing the image in the negative to a sufficiently small size, extremely small positive images of a size approaching the order of magnitude of a microphotograph can be produced in the glass with remarkable clarity. Moreover, in the glasses of my invention, the transparency of portions which are intended to be transparent after "development" far exceeds that of prior photographic media.

From the foregoing it will now be clear that an image of anything which can be photographed can be reproduced in my glasses and that the term "photographic image," as used herein, is intended to include not only portraits, landscapes, etc., but also photographic reproductions of all sorts of drawings, sketches, cartoons and the like.

It is to be understood that the photosensitivity discovered by me in the glasses of my invention differs from, and the term as used herein excludes, the so-called solarization effect which has long been recognized as common to glasses containing manganese or iron. The discoloration of glass by solarization appears during irradiation but is not permanent and may be destroyed by heating the glass. The coloration of my photosensitive glass, on the other hand, does not appear during irradiation but is developed only by heating the irradiated glass at temperatures below its softening point. Such heat-developed coloration cannot be destroyed by such heating. Although some solarization, visible as a slight discoloration, may occur during irradiation of my new glasses, it is not permanent and is removed when the glass is heated to develop the coloration which is latent in the glass as a result of its irradiation.

The term "oxidized silicate glass," as used in the claims, means a glass prepared by fusion of raw glassmaking materials under oxidizing conditions, preferably in the presence of an oxidizing agent such as $NaNO_3$ or KNO_3, containing on the oxide basis a major proportion of silica and a minor proportion of an alkali metal oxide such as sodium oxide, preferably containing a minor proportion of an oxide of a metal other than cadmium of the second periodic group up to and including barium, and optionally containing a minor proportion of one or more other conventional glass-forming oxides such as Al_2O_3, B_2O_3, and PbO, but being free of constituents which inhibit photosensitivity including compounds of arsenic, antimony, cadmium, uranium, thallium, copper, iron, vanadium, manganese, and selenium and also over 6% Al_2O_3, over 5% B_2O_3, and over 3% PbO.

I claim:

1. A photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, and CeO_2 in an amount up to 0.05%.

2. A photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, and SnO_2 in an amount up to 0.02%.

3. An article comprising a body of irradiated, substantially colorless photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, said glass body containing within its mass a predetermined latent photographic image capable of being developed, by uniform heating of the entire glass body, into a visible colored image exhibiting photographic detail.

4. An article comprising a body of irradiated, substantially colorless photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, and CeO_2 in an amount up to 0.05%, said glass body containing within its mass a predetermined latent photographic image capable of being developed, by uniform heating of the entire glass body, into a visible colored image exhibiting photographic detail.

5. An article comprising a body of irradiated, substantially colorless photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, and SnO_2 in an amount up to 0.02%, said glass body containing within its mass a predetermined latent photographic image capable of being developed, by uniform heating of the entire glass body, into a visible colored image exhibiting photographic detail.

6. An article comprising a glass body made of a photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, selected portions of said glass body being colored by the gold to form within its mass a heat-stable image exhibiting photographic detail.

7. An article comprising a glass body made of a photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, and CeO_2 in an amount up to 0.05%, selected portions of said glass body being colored by the gold to form within its mass a heat-stable image exhibiting photographic detail.

8. An article comprising a glass body made of a photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, and SnO_2 in an amount up to 0.02%, selected portions of said glass body being colored by the gold to form within its mass a heat-stable image exhibiting photographic detail.

9. The method of making a glass article which comprises forming an article of a substantially colorless photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, exposing an area of the article to short-wave radiations and thereafter heating the article uniformly for a time and at a temperature sufficient to develop color in the exposed area.

10. The method of making a glass article which comprises forming an article of a substantially colorless photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, and CeO_2 in an amount up to 0.05%, exposing an area of the article to short-wave radiations and thereafter heating the article uniformly for a time and at a temperature sufficient to develop color in the exposed area.

11. The method of making a glass article which comprises forming an article of a substantially colorless photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, and SnO_2 in an amount up to 0.02%, exposing an area of the article to short-wave radiations and thereafter heating the article uniformly for a time and at a temperature sufficient to develop color in the exposed area.

12. The method of making a glass article which comprises forming an article of a substantially colorless photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, exposing an area of the article to short-wave radiations of a given intensity, exposing another area of the article to short-wave radiations of a different intensity, and thereafter heating the article uniformly for a time and at a temperature sufficient to develop color in the exposed areas.

13. The method of making a glass article which comprises forming an article of a substantially colorless photosensitive glass consisting essentially of an oxidized silicate glass containing on the oxide basis by weight about 0.01% to about 0.03% of gold computed as Au, exposing selected areas of the article to short-wave radiations, heating the article uniformly for a time and at a temperature sufficient to develop color in the exposed areas, thereafter exposing hitherto unexposed areas to short-wave radiations and thereafter again heating the article uniformly for a time and at a temperature sufficient to develop color in the subsequently exposed areas.

STANLEY DONALD STOOKEY.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
332,294	Shirley	Dec. 15, 1885
337,170	Libbey	Mar. 2, 1886
343,823	Libbey	June 15, 1886
366,364	Atterbury	July 12, 1887
703,512	Zsigmondy	July 1, 1902
1,169,571	Rosenthal	Jan. 25, 1916
1,271,652	Bellamy	July 9, 1918
1,475,473	Drescher	Nov. 27, 1923
1,771,435	Gelstharp	July 29, 1930
2,049,765	Fischer	Aug. 3, 1936
2,068,801	Hood	Jan. 26, 1937
2,097,275	Fischer	Oct. 26, 1937
2,237,042	Truby	Apr. 1, 1941
2,241,950	Huniger et al.	May 13, 1941
2,306,626	Huniger et al.	Dec. 29, 1942
2,326,012	Dalton	Aug. 3, 1943
2,422,472	Dalton	June 17, 1947

FOREIGN PATENTS

Number	Country	Date
22,306	Germany	1883
205,381	Great Britain	1923
571,017	Germany	1933