

1

3,623,866

STABILIZATION OF PHOTOCROMIC COPY

Alexander Averbach, Skokie, Ill., assignor to

A. B. Dick Company, Niles, Ill.

No Drawing. Filed Nov. 1, 1968, Ser. No. 772,800

Int. Cl. G03c 5/24

U.S. Cl. 96—48

4 Claims

ABSTRACT OF THE DISCLOSURE

The stabilization of copy produced by exposure of a photochromic layer formed of heteropoly acids of molybdenum and tungsten and a reducing agent wherein the layer after exposure is wet with an aqueous alkaline solution of an alkaline material.

The sensitivity of such photochromic systems to light and depth of shades developed has been found to depend, at least in part, on the nature of the reducing substance or substances employed in the system.

In my copending application Ser. No. 772,799 filed concurrently herewith, and entitled "A Photochromic Element," description is made of the marked improvement in color intensity as well as stability of the image formed upon exposure to ultra-violet light by the modification of the photochromic coating to include a phenylglycolic acid or derivative thereof.

It has been found, however, that such photochromic coatings, especially when formulated to increase the sensitivity to light, as by the inclusion of such phenylglycolic acids or derivatives, are subject to the development of background color, as by blackening or coloring of the otherwise white non-imaged portions of the sheet, when the imaged sheet is exposed to natural or artificial light for a short period of time. Blackening of the background occurs more rapidly when exposed to direct sunlight or rays having a substantial amount of ultra-violet.

It is an object of this invention to provide a method for stabilization of a photosensitive sheet of the type described against the development of background color in response to light exposure and it is a related object to provide a method and means for stabilization of the photochromic sheet whereby the non-imaged portions of the sheet resist discoloration during light exposure and otherwise remain white for maximizing the contrast between the developed image and the background.

Tungstic and molybdic heteropoly acids which may be used in the practice of this invention are illustrated in Patent No. 2,981,622, which is incorporated hereby by reference, namely: silico-12-tungstic acid, $H_4SiW_{12}O_{40}$, boro-12-tungstic acid, $H_5BW_{12}O_{40}$, phospho-12-tungstic acid, $H_3PW_{12}O_{40}$, phospho-9-tungstic acid, $H_3PW_9O_{31}$, phospho-12-molybdic acid, $H_3PMo_{12}O_{40}$, silico-12-molybdic acid, $H_4SiMo_{12}O_{40}$, phospho-12-tungstomolybdic acids, $H_3PW_2Mo_3O_{40}$. The heteropoly acids may be used singly or in admixture with each other. The term "heteropoly acid" is here used generically and includes both free acids and their salts in which one or more of the hydrogen ions shown in the formulae above have been replaced by another cation, usually an alkali metal ion. These salts are themselves acid in solution.

As reducing agents, use can be made of the agents described in the aforementioned issued patent and preferably dextrose, stannous chloride, hydroquinone, hydroquinone monoethyl ether, ascorbic acid, benzoin, desoxybenzoin, phenyl hydrazine, alpha bromophenyl acetic acid, gluconic, maleic, citric, adipic, lactic, tartaric and succinic acids, and more preferably phenylglycolic acid derivatives such as described in the aforementioned copending application, including mandelic acid, benzoic acid,

2

methyl mandelate, methenamine mandelate and benzylamine mandelate.

As binders for the coating, use is made of various film formers such as polyvinyl butyral, polyvinylacetate, chlorinated rubber, polyvinyl pyrrolidone, polyacrylamide, gelatin, polyvinyl alcohol and vegetable gums.

It has been found that the discoloration of the background or non-imaged portions of the sheet and particularly the blackening that is experienced with the photochromic systems, the light sensitivity of which has been increased by the presence of phenylglycolic acids and derivatives, can be overcome by stabilization of the background by passing the paper, after exposure to produce copy, through an aqueous alkaline bath. A suitable aqueous alkaline bath can be formulated by solution of an alkaline base material in aqueous medium in which the alkaline base material may be represented by the following:

- (1) salts of a weak acid and a strong base
- (2) ammonium hydroxide
- (3) a quaternary ammonium compound

The above may be illustrated by the following examples:

EXAMPLE 1

5-15% and preferably 8-10% by weight of sodium or potassium carbonate, with the remainder water.

EXAMPLE 2

9-27% by weight of ammonium hydroxide, with the remainder water.

EXAMPLE 3

5-15% and preferably about 10% by weight of tetraethylammonium hydroxide, with the remainder water.

Photochromic coatings which are suitable in the practice of this invention are described in the aforementioned issued U.S. patents and in the aforementioned copending application.

Treatment of the photochromic coating after development with the alkaline solution to stabilize the copy against blackening and discoloration in the non-imaged portions can be made by wetting the copy after exposure with one of the solutions of Examples 1 to 3, by swabbing the surface after exposure with a cotton pad wet with the solution.

In another example, in which a base sheet has a photochromic coating formulated of 9.5% by weight polyvinyl alcohol, 14% by weight phosphotungstic acid and 7% by weight mandelic acid, exposure was made to ultra-violet through a negative to produce copy. One-half of the exposed sheet was swabbed with a 26-28% by weight ammonium solution in water and dried. The dried imaged sheet was thereafter exposed to light for one-half hour. The swabbed portions did not blacken or discolor whereas the portions that were not swabbed turned grey in the background.

It was somewhat surprising that corresponding stabilization effects are incapable of being secured by treatment of the surface with dry ammonium gas, organic amines, or solutions of salts of strong inorganic acids and bases. It was also found that strong bases, such as sodium hydroxide, even in such dilute solutions as 1-2% by weight, adversely affect the image.

Treatment in accordance with the practice of this invention results in copies which can be exposed for eight to ten weeks in ambient light without appreciable change in background.

It will be apparent from the foregoing that I have provided a simple and efficient means for stabilization of photochromic copies against discoloration in the background in response to light exposure whereby more per-

manent copy of good copy quality can be achieved by such photochromic techniques.

It will be understood that changes may be made in the details of formulation and operation without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. The method of producing a stabilized photochromic copy comprising exposing a copy sheet having a photochromic coating formed of a heteropoly acid of molybdenum and tungsten and a reducing agent for the development of color change in the exposed portions, wetting the surface of the photochromic coating with an aqueous alkaline solution consisting essentially of an alkaline material selected from the group consisting of the salt of a weak acid and a strong base, ammonium hydroxide and a quaternary ammonium compound and water after exposure to stabilize the non-imaged portions of the coating against discoloration.

2. The method as claimed in claim 1 in which the reducing agent is a phenyl glycolic acid or derivatives thereof.

3. The method as claimed in claim 1 in which the photochromic compound is selected from the group consisting of tungstic and molybdic acid and complex formed thereof with phosphoric, boric or silicic acid.

4. The method as claimed in claim 1 in which the alkaline material is selected from the group consisting of a salt of a weak acid and a strong base present in solution in an amount within the range of 5-15% by weight, 9-27% by weight ammonium hydroxide, and a quaternary ammonium compound present in solution in an amount within the range of 5-15% by weight.

References Cited

UNITED STATES PATENTS

1,934,451	11/1933	Sheppard et al.	95—7
2,427,443	9/1947	Cochran	95—7
2,855,300	10/1958	Chalkley	96—48
2,895,892	7/1959	Chalkley	204—157
2,915,392	12/1959	Pedersen	96—27
2,981,622	4/1961	Chalkley	96—48
3,169,064	2/1965	Levy	96—27
3,236,651	2/1966	Marks et al.	96—88
3,285,746	11/1966	Marks et al.	96—90
3,293,037	12/1966	Chopoorian	96—90
3,322,542	5/1967	Fisherullman	96—90
3,322,552	5/1967	Roberts et al.	23—50 X
3,361,706	1/1968	Meriwether et al. ..	96—90 PC

FOREIGN PATENTS

658,273	6/1965	Belgium	96—90 PC
727,559	2/1966	Canada	96—90 PC
736,192	11/1932	France	96—90

OTHER REFERENCES

Meriweather, Journal of the American Chem. Soc., vol. 87, No. 20, Oct. 20, 1965, p. 4441-4454.

WILLIAM D. MARTIN, Primary Examiner

B. D. PIANALTO, Assistant Examiner

U.S. Cl. X.R.

96—90; 252—300

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,623,866 Dated November 30, 1971

Inventor(s) Alexander Averbach

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, after line 17, insert

This invention relates to a photographic process for producing images by photosensitive inorganic photochromic or phototropic substances which acquire a color change upon exposure to light.

Photochromic compounds may be subdivided into organic substances represented by spyrans and inorganic substances represented by heteropoly acids of tungsten and molybdenum, such as phospho-tungstic and phospho-molybdic acids.

This invention has to do with the latter group of inorganic photochromic compounds and their utilization in the production of images by reason of their longer reversion periods, as is or in stabilized form, whereby they are better adapted for print-out and other copy processes. The sensitivity of such inorganic heteropoly acids of tungsten and molybdenum are greatly increased when employed in the form of tungstic and molybdic complexes with phosphoric, boric or silicic acids, including mixtures of such tungstic and molybdic complexes.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,623,866 Dated November 30, 1971

Inventor(s) Alexander Averbach PAGE - 2

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Photochromic compounds and complexes thereof and their utilization in photosensitive products are well known to the art. Reference may be made to the following United States patents: No. 1,934,451; No. 2,427,443; No. 2,895,892; No. 2,981,622; No. 3,169,064; No. 3,236,651; No. 3,285,746; No. 3,293,037 and No. 3,322,552. Such photochromic processes and compositions have not experienced widespread usage in the copy field because of the inability to obtain colors and hues sufficiently deep for a desired color contrast. Furthermore, systems of the type heretofore employed have been characterized by too rapid reversion after removal of the ultra-violet light whereby the image remains for only a relatively short period of time.

Signed and sealed this 20th day of June 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents