United States Patent Office 2,813,792
Patented Nov. 19, 1957

2,813,792

PHOTOSENSITIVE MATERIAL

Oskar Süs and Wilhelm Neugebauer, Wiesbaden-Biebrich, and Hans Böttger, Fritz Endermann, and Werner Schäfer, Wiesbaden, Germany, assignors, by mesne assignments, to Keuffel & Esser Co., Hoboken, N. J., a corporation of New Jersey

No Drawing. Application March 19, 1953, Serial No. 343,502

Claims priority, application Germany March 27, 1952

14 Claims. (Cl. 96—75)

This invention relates to light sensitive material of the type usually sensitized with water soluble light sensitive substances such as used for making diazotypes, blueprints and Vandyke prints or brownprints. In particular the invention relates to a carrier layer for these light sensitive substances applied to the surface of an absorbent base material and made up of particles formed of silicates of metals of the second group of the periodic system.

Patent No. 2,433,515 discloses that a layer of silica particles applied as a precoat for blueprint paper and similar light sensitive materials greatly improves the prints obtained from these materials.

The objects of the present invention are to achieve all the advantages of the silica precoated material and at the same time produce prints which have greater fastness to ink and India ink and which are more receptive to water colors. The ink or color does not bleed or feather and the India ink will not peel or crack off.

The light sensitive materials to which the present invention relates are conventionally applied to an absorbent base material, generally paper, although other absorbent bases such as cardboard, cloth and other textile fabrics and the like may be employed. The layer of metal silicate particles applied to the absorbent base material according to the present invention should not be confused with a sizing. Sizing is ordinarily applied to paper for example as a step in the paper making process before the web is fully matted into a sheet. Thus these sizings penetrate through the entire thickness of the sheet whereas the discrete particles applied according to the present invention form a layer at the surface of the sheet. Usually the absorbent sheet treated according to the present invention will have been previously sized since the papers conventionally used for diazotype prints, blueprints and the like are normally sized papers.

As is known in the art, diazotype materials have been made by coating a light sensitive diazo compound from an aqueous solution onto the surface of an absorbent base material such as described in the previous paragraph. In two component diazotype materials, an azo dye coupling component is coated with the light sensitive diazo compound and after exposure through a pattern an image is formed by exposing the sheet to ammonia fumes which causes the undecomposed diazo compound to couple with the coupling component to form an azo dye image. In one component diazotype materials, the azo component is not coated on the sheet with the light sensitive diazo compound but is applied after exposure in an alkaline solution. Blue print coatings consist essentially of a light sensitive ferric salt and a water soluble complex iron cyanide salt. Exposure to actinic light results in reduction of the ferric salt to a ferrous salt in the light struck areas. Application of water after exposure results in the formation of an insoluble blue complex from the ferrous salt and the water soluble iron cyanide salt. Vandyke or brownprints also depend on

the light reduction of light sensitive ferric salts but in this case the ferrous salt which is formed reduces a water soluble silver salt such as silver nitrate to metallic silver which forms a brown or black image.

According to the present invention, a layer of metal silicate particles may be applied to the base material used for making photosensitive materials of any of the types previously described in order to obtain prints of improved color and contrast with the additional advantages previously noted. Of the metals of the second group of the periodic system, magnesium and the alkaline-earth metals are particularly suitable. The particles applied to the paper are preferably of colloidal size and are dispersed in water or an aqueous solution which may be coated onto the surface of the absorbent base material by known methods and dried. The terms "minutely dispersed" and "particles of colloidal size" as used herein are intended to include particles having a size up to 5μ, the best size being between $.1\mu$ and 1μ.

It is advantageous to produce the silicate layer according to the present invention on the base material by means of minutely dispersed aqueous suspensions of the silicates which have been prepared by causing a reaction to take place in an aqueous medium. Silicate suspensions which give good results can be obtained for example by mixing, while thoroughly stirring, dilute sodium silicate solutions with dilute aqueous solutions of the salts of elements belonging to the second group of the periodic system. Silicates of elements in the 3rd group in the periodical system, which may function as metals and are able to form salts on reaction with acids may also be used according to the invention. Before applying the silicate suspensions thus obtained the mother liquor can be centrifuged off. By adding water to the moist remainder of silicate the fluid component of the suspension can be restored. This suspension is suitable for coating on paper or the like. The dispersion or suspension used for coating should contain 1 to 10% solids, preferably 3 to 5%, of the particular silicate.

In practicing the present invention it is possible to first, as a separate step, coat the silicate layer on the base material and then on top of the silicate layer coat the light-sensitive components. However, it is also possible to combine a solution of the light-sensitive substance with the silicate suspension and apply the mixture onto the surface of the support. The layer thus formed is subsequently dried.

The following examples are inserted in order to illustrate the present invention. It is not intended to limit the scope of the invention to the content of the examples.

(1) In a conventional paper coating machine, paper stock of the type used as base material in manufacturing light-sensitive diazotype paper is coated with a 4% aqueous suspension of magnesium silicate and subsequently dried. Upon elimination of the water and drying of the silicate layer, a diazotype sensitizing soluton including conventional diazo compounds and coupling components for forming black lines is coated onto the silicate layer in a similar coating machine or a double coating machine may be used for applying both coatings. When dried, the light-sensitive paper is exposed to light under a positive master and, upon its development, it yields a jet black, velvety copy that readily accepts inscriptions with ink, India ink or coatings of water colors.

The silicate suspension is obtained by the following process: 400 parts of an approximately 55% solution of crude sodium silicate (a suitable product of this kind is sold under the trade name "Natronwasserglas" 58/60° Bé by the firm "Rheinische Wasserglasfabriken" at Ludwigshafen on Rhine) are diluted with 2,400 parts of water. This solution is thoroughly swirled around by

means of an electric mixer (i. e. a high-speed mixer for example of 2800 R. P. M.) and 480 parts of commercial magnesium chloride-6-hydrate dissolved in 2,000 parts of water are added at room temperature as quickly as possible, within a few seconds. The magnesium silicate thus formed is deposited as a very fine-grained, uniformly distributed sediment which is ready for use in this form.

Instead of the above-mentoned 4% aqueous suspension of magnesium silicate the following suspension can also be used for producing the silicate layer on the backing paper:

600 parts of crude magnesium chloride-6-hydrate are dissolved in 5,000 parts of hot water (60° C.) and, while intensively stirring, within 5 minutes 500 parts of an approximately 55% sodium silicate solution dissolved in 4,000 parts of hot water (60° C.) are added. The magnesium silicate precipitates in a very finely dispersed state and is separated from the mother liquor by means of a centrifuge. The residual white paste is treated with fresh water to make 5,620 parts. After renewed mixing (for approximately 10 minutes) by means of the high-speed mixer, a 4% magnesium silicate suspension having a thixotropic character is formed which may be used for coating paper. Subsequently the coated paper may be made sensitive to light by coating it with a conventional blueprint sensitizing solution including a light sensitive ferric salt and a water soluble iron cyanide salt such as potassium ferricyanide. The light-sensitive blue-print paper affords prints prepared in this manner of excellent contrast and excellent legibility even from poor originals, such as bad pencil drawings. Such prints have a rich deep blue color.

Either of the aforementioned magnesium silicate dispersions may also be added directly to the sensitizing solution and applied to the paper therewith. This procedure results in prints having similar properties to those described above.

(2) Instead of the magnesium silicate suspension described in Example 1, an aqueous calcium silicate suspension can also be used for the production of the precoat layer applied directly on the paper stock. The calcium silicate suspension is prepared by diluting 225 parts of a technical sodium silicate solution of 58/60° Bé with 2,000 parts of water and, by adding very quickly, while stirring thoroughly as described in Example 1, a solution of 111 parts of calcium chloride in 1,000 parts of water. The calcium silicate deposits in a gel-like state which is separated from the mother liquor in a centrifuge. The paste thus obtained is treated with fresh water to make 2,870 parts and made suitable for coating purposes by stirring this intensively.

Paper precoated with this suspension and subsequently rendered sensitive to light by means of a diazo-type sensitizing solution of the usual type for forming blue images which may be developable by either the dry or semi-wet method has proved to afford, upon exposure to light under a master, prints that show a deeper and stronger color shade than those produced on paper which is not provided with the calcium silicate layer.

(3) Analogously to the previous examples, paper stock may be coated with an aqueous zinc silicate suspension and made sensitive to light with any of the water soluble light sensitive substances after drying the silicate layer. This paper, too, produces prints of excellent contrast. Inscriptions with ink and India ink will not bleed when applied to this type of paper.

Production of the zinc silicate suspension is analogous to that of the calcium silicate, described in Example 2. 140 parts of the zinc chloride are mixed with 225 parts of the sodium silicate solution 58/60° Bé. The gel-like zinc silicate deposit is centrifuged from the mother liquor and transformed into a coatable suspension by adding 3,750 parts of fresh water and stirring vigorously.

(4) Transparentized paper or paper stock which can be used for intermediate reproductions or duplicate originals and which transmits long wave ultraviolet rays in the production of subsequent prints, is precoated with a magnesium silicate suspension prepared as follows:

850 g. of crystallized sodium-meta-silicate-9-hydrate Na_2SiO_3—$9H_2O$) are dissolved in 5 liters of water and heated to 85°–90° C. A solution of 400 g. magnesium-chloride-6-hydrate (technically pure) in 4 liters of water is added during a period of 3 hours with high speed stirring and thorough mixing. After the magnesium silicate has formed, the reaction mixture is stirred for another hour at a temperature of 85°–90° C. A suspension is obtained which is slowly cooled down while stirring and then preferably left standing for 1 or 2 days. The magnesium-silicate-gel is subsequently separated from the salt-bearing mother liquor by means of a clearing centrifuge with at least 3000 R. P. M. 1800 g. to 1850 g. of a paste is obtained which is dispersed in fresh water (3750–3800 g.) and mixed in a high-speed mixer (3000 R. P. M.) to form a suspension (total weight 5600 g.). The suspension, which still has a pH-value of 10 is brought down to a pH-value of 8.0 to 8.2, by slowly adding an 18% solution of hydrochloric acid free from iron. Then process, for which about 100–105 cc. of an 18% solution of hydrochloric acid are used, takes place in a high-speed mixer under steady control. To the magnesium-silicate (-hydrosilicate)—suspension thus obtained, 1.0% of a water-soluble cellulose-ether of high viscosity is added, e. g. methyl-cellulose or oxethylmethylcelluose. After the cellulose-ether is dissolved, the suspension is ready for coating.

It may be advantageous to add to the silicate suspension also other natural or synthetic organic colloidal substances, such as gelatine, casein, dextrin, water soluble synthetic resins, e. g. polyvinyl-alcohol or polyvinyl-pyrrolidone, or water insoluble synthetic resins, suitably in finely dispersed state. Through the addition of these substances, the single silicate particles are cemented to each other which helps to prevent the light-sensitive solutions from penetrating into the base material. Very small quantities of the additional substances are sufficient.

In order to render them light-sensitive, the transparentized paper thus pretreated is coated with one of the usual diazotype preparations which develops brown azo dyes. The paper is then dried. The prints thus obtained yield better contrasts than those obtained from not-pretreated papers, and their printing density is higher, which is very important when the print is intended as an intermediate for the production of subsequent copies.

If solid sodium-meta-silicate of a constant constitution (molar proportion: $Na_2O:SiO_2=1:1$) is used to prepare the silicate suspension, after the precipitation, the surplus alkali must be neutralized with a strong acid or its ammonium salt, in order not to impair the keeping quality or storability of the paper after it is coated with a diazo preparation.

(5) Very good prints are obtained if the light-sensitive paper is precoated according to Example 4 with a magnesium silicate suspension which is prepared as follows:

In a closed 50 liter vessel with two high-speed mixers, 1960 g. of magnesium-chloride-6-hydrate $MgCl_2$—$6H_2O$ (technically pure) are dissolved in 16 liters of water and heated to 85°–90° C. While the solution is stirred rapidly, a solution of 2550 g. of crystallized sodium-meta-silicate-9-hydrate Na_2SiO_3—$9H_2O$ (technically pure) in 12 liters of water is added in a steady stream over a period of 4 hours. After the magnesium-silicate has precipitated, the contents of the vessel are stirred for another hour. Subsequently, 900 g. of technical ammonium-chloride are added and the suspension is kept boiling for another hour with constant mixing and stirring. During this time, one of the outlets of the container is opened to let the ammonia gas escape. While the reaction mixture cools down, it is stirred for another 4 hours. The

suspension thus obtained is kept standing for 50 to 65 more hours. The magnesium-silicate-gel is separated from the salt-bearing mother liquor by means of a centrifuge with at least 3000 R. P. M. Approximately 5200 to 5500 g. of a paste is agitated with 9500–9800 g. of water to yield 15 kg. of a homogeneous suspension. This suspension (which is now ready for coating) has a pH-value of 8.0 to 8.4 (potentiometrically measured).

Analogously to the preceding examples, an ordinary diazotype base material (paper) is pre-coated with this silicate suspension and subsequently coated with a light-sensitive layer diazo preparation. Prints obtained from material thus prepared show distinctly better contrasts than those made with material which was not pre-treated.

Finely dispersed silica may be added to this silicate suspension, as well as to all silicate suspensions covered by the present invention. For example a silica suspension of the kind described in U. S. Patent 2,433,515 may be used. However, prints obtained from diazotype material prepared with such suspensions show an inferior fastness to ink.

(6) If, on preparing a silicate suspension according to Example 3, an equivalent quantity of aluminum-sulfate is used instead of zinc-chloride, an aluminum silicate-gel is obtained which can be coated on a paper sheet after being separated from the mother liquor in a centrifuge and then diluted with water.

If coupling components are used in the light-sensitive preparation which have a tendency to form aluminum lakes, e. g. compounds containing hydroxyl-groups in ortho-position to each other, such as 2,3-dihydroxynaphthalene and derivatives thereof, formation of an aluminum silicate layer beneath the light-sensitive layer is less advisable. In all other cases, if, for example, resorcinol, 2 - hydroxynaphthalene - 3,6 - disodiumsulfonate or 2,7-dihydroxynaphthalene-3,6-disodiumsulfonate is used as a coupling component, good prints with excellent contrasts are obtained.

Having thus described the invention, what is claimed is:

1. Photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles formed of a silicate of a metal of the second and third groups of the periodic system, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive compound selected from the group consisting of diazo compounds and ferric salts.

2. Photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles formed of a silicate of a metal of the second group of the periodic system selected from the group consisting of magnesium and the alkaline earth metals, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive compound selected from the group consisting of diazo compounds and ferric salts.

3. Photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles formed of a silicate of a metal of the second group of the periodic system selected from the group consisting of magnesium, calcium and zinc, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive compound selected from the group consisting of diazo compounds and ferric salts.

4. Photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles formed of magnesium silicate, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive compound selected from the group consisting of diazo compounds and ferric salts.

5. Photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles formed of calcium silicate, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive compound selected from the group consisting of diazo compounds and ferric salts.

6. Photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles formed of zinc silicate, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive compound selected from the group consisting of diazo compounds and ferric salts.

7. Photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles formed of aluminum silicate, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive compound selected from the group consisting of diazo compounds and ferric salts.

8. Diazotype photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles formed of a silicate of a metal of the second and third groups of the periodic system, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive diazo compound.

9. Diazotype photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles formed of a silicate of a metal of the second and third groups of the periodic system, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive diazo compound and an azo dye coupling component.

10. Blueprint photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles formed of a silicate of a metal of the second and third groups of the periodic system, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive ferric salt and a complex iron cyanide salt.

11. Photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles formed of a silicate of a metal of the second and third groups of the periodic system, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive ferric salt and a water soluble silver salt.

12. Photoprinting material comprising an absorbent base coated with a carrier layer consisting essentially of particles of collodial size formed of a silicate of a metal of the second and third groups of the periodic system, said carrier layer being sensitized with a photosensitive solution comprising a light sensitive compound selected from the group consisting of diazo compounds and ferric salts.

13. The method of making photoprinting material comprising the steps of coating an absorbent base with a carrier layer consisting essentially of particles formed of a silicate of a metal of the second and third groups of the periodic system and coating said layer of particles on said base with a photosensitive solution comprising a light sensitive compound selected from the group consisting of diazo compounds and ferric salts.

14. The method of making photoprinting material comprising the step of applying to an absorbent base a coating consisting of an aqueous solution containing a light sensitive compound selected from the group consisting of diazo compounds and ferric salts and dispersed particles formed of a silicate of a metal of the second and third groups of the periodic system.

References Cited in the file of this patent

UNITED STATES PATENTS

2,178,771	Alink et al.	Nov. 7, 1939
2,626,867	Webster	Jan. 27, 1953