March 2 1943. W. C. TOLAND ET AL 2,312,854

LIGHT-SENSITIVE ELEMENT

Filed July 20, 1940

Fig. 1.

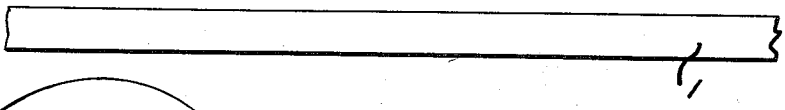


Fig. 2.

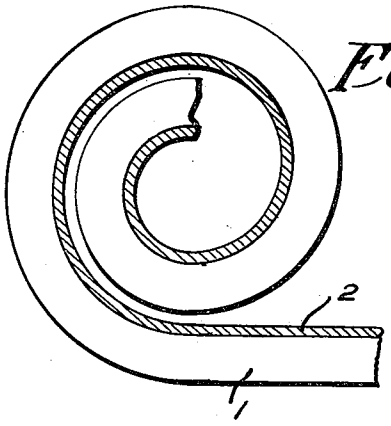


Fig. 2a

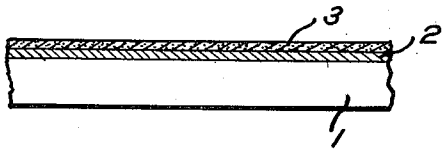


Fig. 3.

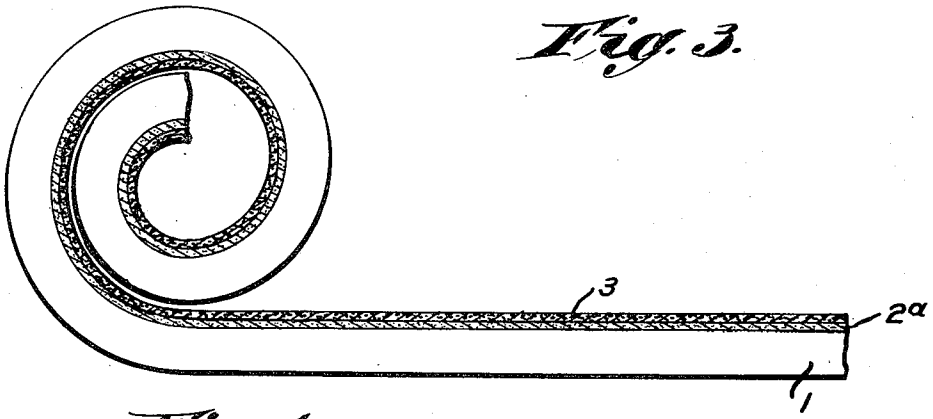
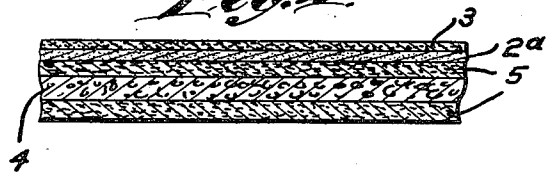


Fig. 4.



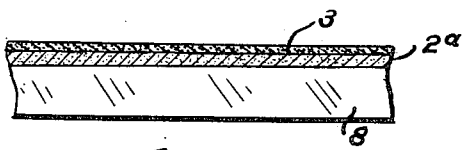


Fig. 5.

Inventors
William C. Toland
Ellis Bassist
Munroe H. Hamilton
By
Attorney

Patented Mar. 2, 1943 2,312,854

UNITED STATES PATENT OFFICE

2,312,854

LIGHT-SENSITIVE ELEMENT

William Craig Toland and Ellis Bassist, Brookline, Mass., assignors to William Craig Toland, Brookline, Mass., as trustee

Application July 20, 1940, Serial No. 346,514

8 Claims. (Cl. 95—8)

This invention relates to light-sensitive elements and more especially to light-sensitive elements in which photosensitive coatings or emulsions are associated with printing plate members.

Photosensitive emulsions and coatings may be considered as of two general types; those which are darkened and rendered more opaque by exposure to light and subsequent development; and those which, normally soluble in water, become insoluble therein upon exposure to light. The first type is utilized to make photographic negatives and consists of emulsions as of gelatin and silver haloids. The second type of light-sensitive element is used to make printing plates and is illustrated by bichromated colloids such as albumin which requires actinic light for exposure. Neither type can be satisfactorily applied to a printing plate and held sensitive. The bichromated colloid type of light-sensitive material rapidly loses sensitivity and must be used at, or very shortly after, the time is coated on the plate element.

A principal object of the invention is to improve light-sensitive elements and to devise as an article of manufacture a light-sensitive product which can be prepared and held active for extended periods and thereafter processed to make planographic printing plates. Another object is to increase the period during which coatings of colloids and chromic salts may be held sensitive, with a view to employing them in the making of planographic and other types of printing plates and also photographic negatives. The invention further aims to provide as an article of manufacture a continuous web of printing plate material having light-sensitive coatings associated therewith; to effect savings in the cost of preparation of light-sensitive elements; and to eliminate some of the equipment and procedures now required in the preparation of such products.

Attainment of these and other objects of the invention will appear in the following description of the drawing and discussion relating thereto.

In the accompanying drawing:

Figure 1 is a fragmentary side elevation of a printing support employed in making a light-sensitive element of the invention.

Fig. 2 is a view in side elevation illustrating a coating step in a method of making a light-sensitive printing element.

Fig. 2*a* is an elevational view illustrating another coating step in the method referred to, and further indicating one form of light-sensitive printing plate material.

Fig. 3 is a view in side elevation illustrating another form of light-sensitive printing plate material.

Fig. 4 is a fragmentary cross section illustrating a modification of light-sensitive element.

Fig. 5 is another fragmentary cross sectional view illustrating still another modification.

Referring in detail to the drawing, Figs. 1–3 relate to a light-sensitive element of the bichromated colloid type which is adapted to provide a planographic printing plate; and Figs. 4 and 5 indicate modifications of light-sensitive elements.

It is customary in making printing plates of the photo-lithographic class to employ light-sensitive coatings or emulsions in forming greasy printing images. A support, usually of metal, is provided with a grained surface which will retain moisture by capillary attraction. The support is covered with a thin coating of a mixture such as albumin and ammonium bichromate which, upon exposure to actinic light, passed through a negative, is hardened in selected areas. Thereafter, the unhardened portions of the coating are washed away in water and the hardened portions are rendered grease-receptive to form a printing image which will accept greasy ink. The mixture of bichromated colloid must be used while fresh as it forms a very unstable product which tends to "expose itself out" and lose all sensitivity to light.

In accordance with the invention, the tendency of a printing plate colloid, such as bichromated albumin, to lose its sensitivity is greatly reduced by associating the colloid with suitable protective bodies. As illustrative of one suitable procedure, a lithographic printing plate support **1** is provided as shown in Fig. 1. On the support **1** is applied a layer **2** of a protective body which is of an absorbent colloidal-like character and water-soluble. Thereafter a light-sensitive coating **3**, made up of a mixture of ammonium bichromate and albumin, is uniformly spread over the layer **2** and allowed to penetrate into it.

The bichromated albumin constituting the light-sensitive coating, when dispersed in a protective body or layer as described, is prevented, to a very substantial extent, from reacting within itself, and becomes a light-sensitive medium of substantially constant nature. The immediate result of this is to make possible the manufacture of a light-sensitive element which can be held sensitive for periods of several weeks and longer, and then successfully exposed to form a planographic printing plate. For example, in accordance with the albumin process, a sensitized plate material, previously prepared as noted, may be

secured adjacent a photographic negative member, exposed to actinic light and rolled up with a greasy developing ink. The inked surface is lightly rubbed under running water to wash away both the unexposed portions of the bichromated albumin and those parts of the layer 2 with which such unexposed portions of the albumin are associated. This leaves, on the surface of the plate material, a grease-receptive printing image made up of hardened bichromated albumin and portions of the layer 2 which have become incorporated with the hardened albumin.

The support 1 may be formed of metals, resin materials, papers and other substances, and is intended to be generally illustrative of various lithographic printing surfaces as lithographic stone, conventional grained metal such as zinc and aluminum, and other prepared lithographic surfaces. Examples of suitable protective bodies, of absorbent and water-soluble nature, for the layer 2 are casein, gum arabic, gelatin, glue, and other similar materials. The use of chemical agents such as ammonium bichromate, ferric chloride, ferric sulphate, cupric chloride, borax, boric acid, and others, as well as physical agents as heat, may be used if desired to modify the absorption and solubility of the protective materials noted. Other protective bodies, consisting of suitably polymerized materials, may also provide the protective function noted, as for example water soluble resins and the like, and the protective colloid materials indicated may be desired to be mixed with the light-sensitive coating mixtures in either a film or a solution state. In the latter case, an aqueous suspension of the protective colloid may be prepared and a mixture of a light-sensitive coating material such as albumin and water directly added to this suspension.

Various mixtures containing chromic salts, or salts exhibiting properties similar to those of chromic salts, may be employed as the coating 3. The characteristic of a bichromated colloid to react with itself may result in a product which at first is not sensitive to light but develops or acquires sensitivity upon aging. This may occur particularly where only small amounts of ammonium bichromate are used. Therefore it may further be desired to associate, in any of the ways above described, various amounts or solution strengths of chromic salts. The sensitive salt may be desired to be retained in a protective body which is adapted to subsequent formation into printing image portions.

A feature of the invention consists in the application of protected light-sensitive coatings or emulsions to a strip or web of printing plate material as has been diagrammatically illustrated in Figs. 2 and 3. It is pointed out that such a procedure is made possible by the protective means noted whereby bichromated colloid coatings may be kept sensitive for extended periods. There is thus provided a novel and useful printing plate material occurring as an article of manufacture in a roll or continuous sheet form which is adapted to greatly facilitate manufacture, handling, storing and shipping operations.

A preferred embodiment of the invention consists in a light-sensitive mixture partially dispersed in a protective body of hydrophilic material which, in addition to maintaining the mixture sensitive to light, is not soluble in water and is adapted to function as the ink-repellent portions of a lithographic printing surface. A light-sensitive element of this nature has been illustrated in Fig. 3 in which a support as 1 is covered with a layer 2a of a vinyl resin such as polyvinyl alcohol. Other materials of hydrophilic character may be employed as for example synthetic hydrophilic resins, and the like. A photo-sensitive coating 3 as of bichromated albumin may be spread over the hydrophilic layer 2a allowed to partially sink into the layer 2a and be developed to form printing and non-printing portions of a printing plate in the manner above described.

It should be observed that a film of hydrophilic material such as specified, while being water-receptive, is not dissolved in the water used for development of the plate. However, the unexposed bichromated colloid is washed away from, and out of, the hydrophilic absorbent medium while the exposed portions of bichromated albumin are hardened on the hydrophilic material and rendered grease-receptive in the usual manner. The hydrophilic materials may also be hardened or otherwise modified by the use of both chemical and physical agents such as those noted above, and the use of ammonium bichromate with the polyvinyl alcohol noted may be particularly desirable. In this case the hardening action may improve both the protective action of the hydrophilic layer for a bichromated colloid and its water-receptive character.

The hydrophilic layer is particularly adapted to being applied to a web or strip of flexible printing plate material. It is pointed out that the hydrophilic layer also forms a very satisfactory substitute for a lithographic printing surface of grained metal. It may therefore be coated on a non-metallic base and provide a suitable printing plate element. Fig. 4 discloses one form of non-metallic base, or printing plate material, which consists in a number of layers of materials such as paper and resin coatings laminated together to make a flexible, substantially non-stretchable product. Numeral 4 is intended to be illustrative of a paper web laminated with resin layers 5. These resin layers are described in our copending application, Ser. No. 306,141 filed November 27, 1937.

As illustrative of a procedure in which specific amounts and materials are used, the following example is cited, it being understood that this procedure is given by way of example only and is not to be taken in a limiting sense.

On a base of suitable non-stretch character, as the resin and paper just described, is applied a colloidal coating prepared by mixing together a suspension of polyvinyl alcohol and a hardening agent such as ammonium bichromate in the following amounts:

	Ounces
5% polyvinyl alcohol suspension	7
Ammonium bichromate	1

or other amounts in similar proportions. The coating is allowed to dry to form a film which will readily absorb moisture.

A printing plate coating is then prepared by mixing ammonium bichromate and albumin in conventional proportions as employed in the albumin process. This coating is spread over the hydrophilic surface and allowed to become impregnated therein. Upon drying there is obtained a light-sensitive element which may be formed into a printing plate.

It will be seen that there is provided a cheap and efficient light-sensitive product which may be made in a strip or web form. Manufacture of the product in a web form or roll is an advantage since it makes possible the use of high-speed

machinery and the material in this form can be stored and handled very advantageously, with more precise plate sizes being cut off from the roll of material as desired. Graining is eliminated as well as the use of chemicals used in counter-etching, cleaning and mixing of albumin solutions. Still another advantage of the plate material described consists in elimination of the operations usually conducted in the laboratory in preparing a plate. No special machinery or time is required in properly applying a sensitized coating on the plate. No stocks of chemicals, as sensitized salts, or coating colloids, are required to be maintained, and no time is required to be spent in mixing these chemicals. Apparatus, such as whirling plates for distributing these coatings uniformly, blowers, and other mechanisms, are eliminated.

The protective colloid coating of the invention may also be used in other ways than as a printing plate, as has, for example, been illustrated in Fig. 5. In this figure, a sensitized colloid coating 3 is partially impregnated in a protective colloid layer 2*a*, applied to a support 8. In this form of light-sensitive element, the novel feature consists in a support 8 which is made up of translucent materials, as for example, glass, translucent paper, translucent plastic materials, and others. This form of light-sensitive element may be useful as a transparent member for various purposes as a photographic negative, and the like.

The protection of a light-sensitive material by a proper colloid coating may also be utilized to form gravure plates. For example, the sensitized layer may be associated with a metal support which is adapted to be formed into a gravure plate. In this case the permanently sensitive coating may be photographically exposed when desired and then used as a resist in conventional etching procedures.

It should be observed that a novel step is effected in utilizing the bichromate to change the silver to silver chromate and to anchor the silver chromate and gelatin in the hydrophilic base. The hydrophilic support provides a bond for securing the gelatin not possible with supports such as metal or glass or plastic. This bond enables the gelatin printing portions to withstand extended press operation.

It will be seen that various improvements are obtained by the invention, including a light-sensitive printing plate material which can be held sensitive and therefore manufactured and stored on a production basis. The objection heretofore present with respect to the use of chromic salts, due to their tendency to quickly "expose themselves out" has been overcome and emulsions containing such salts may be employed in any type of light-sensitive element where their use may be found desirable.

The term "hydrophilic" as employed in the specification is intended to mean "water-absorptive" and not "water-soluble." Where the material referred to occurs in a powder state or other form which is water-soluble, as for example polyvinyl alcohol and other substances, it is intended that "hydrophilic" refers to such materials in a film or other state in which they are not water-soluble but only water-absorptive.

While we have shown preferred embodiments of the invention, it should be understood that various changes and modifications may be resorted to, in keeping with the spirit of the invention as defined by the appended claims.

Having described our invention, we claim:

1. A light-sensitive product comprising a base, a layer of a hydrophilic polyvinyl alcohol superimposed on the base, said hydrophilic polyvinyl alcohol also being of a water-receptive character suitable for lithographic printing, said layer having a photo-sensitive emulsion coated thereon, the photo-sensitive emulsion including a light-sensitive salt which requires actinic light for exposure, the photosensitive emulsion further including a binder for the light-sensitive salt, said binder being of a type adapted to be hardened to a water-insoluble state upon exposure of the light-sensitive salts.

2. A light-sensitive product comprising a hydrophilic film of polyvinyl alcohol having a photosensitive emulsion of a chromic salt and a binder overlying and impregnated therein, said binder being of a type adapted to be hardened into a substantially water-insoluble state upon exposure of the chromic salt to actinic light.

3. A light-sensitive product comprising a hydrophilic film of polyvinyl alcohol and a hardening agent, said film having coated thereon a light-sensitive material which is soluble in water, said light-sensitive material including a chromic salt and a binder which is adapted to be rendered water-insoluble upon exposure of the chromic salt to actinic light.

4. A light-sensitive product which comprises a layer of a hydrophilic polyvinyl alcohol having superimposed thereon a layer of a chromic salt dispersed in a colloid, said polyvinyl alcohol being effective to prolong the period of light sensitivity of said chromic salt.

5. A light-sensitive product which comprises a support, a layer of hydrophilic polyvinyl alcohol on the support, a second layer of a photosensitive emulsion which includes a chromic salt dispersed in albumin suspension, said photosensitive emulsion being impregnated in the layer of polyvinyl alcohol and said polyvinyl alcohol being effective to prolong the period during which the chromic salt remains sensitive to the action of actinic light.

6. A light-sensitive product comprising a web of flexible material, in roll form, said web having a layer of hydrophilic polyvinyl alcohol, a coating of a photosensitive emulsion, said photosensitive emulsion including a chromic salt and a binder which is adapted to be hardened to a water-insoluble state upon exposure of the chromic salt to actinic light.

7. As an article of manufacture, a strip of material provided with a hydrophilic coating of a hydrophilic polyvinyl alcohol, and a layer of light-sensitive material impregnated in the said coating, said layer being of the type which is hardened to a water-insoluble state upon exposure to actinic light.

8. A light-sensitive element comprising a laminated support which is substantially resistant to shrinking or stretching when subjected to water, a hydrophilic layer of polyvinyl alcohol on said support, a light-sensitive mixture dispersed in said hydrophilic layer, said light-sensitive mixture including a chromic salt and a binder which is rendered water-insoluble upon exposure of the chromic salt to actinic light and said hydrophilic layer adapted to protect the light-sensitivity of the said mixture.

WILLIAM CRAIG TOLAND.
ELLIS BASSIST.