Patented Dec. 26, 1939

2,184,311

UNITED STATES PATENT OFFICE

2,184,311

PHOTOGRAPHIC AND PRINTING MEDIA

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No Drawing. Application June 17, 1937, Serial No. 148,772

12 Claims. (Cl. 95—7)

This invention relates to photographic and printing media. More particularly, it relates to improved light-sensitive compositions and to films, printing surfaces and the like formed therefrom, which are adapted to be used in a variety of photographic and printing processes.

The invention will be described with particular reference to photolithographic printing processes wherein the improved media of the invention possess exceptional utility.

The photolithographic processes now in general use involve printing from a photolithographic plate which comprises essentially a zinc or aluminum plate, on the surface of which the design portions have been rendered receptive to the printing ink while the other portions are non ink-receptive. In the direct printing process, the plate is usually mounted upon a roller which is revolved in contact with two other rollers. One of the latter wets the hydrophilic portions of the plate with an aqueous "fountain solution"; the other roller carries the oily printing ink and applies it to the hydrophobic surfaces of the plate which compose the design. The inked plate is then contacted with the paper or other material to be printed. In the offset printing process, a similar procedure is employed except that the design is first transferred from the lithographic plate to a rubber roller, thence from the latter to the surface to be printed.

The photolithographic plates used heretofore have usually consisted of a zinc or aluminum plate coated with albumen or gelatine, with which is incorporated a light-sensitive agent, such as a dichromate, which is capable of causing hardening of the albumen or gelatine upon exposure to light. To produce the image upon such a plate, it is exposed to ultra-violet light under a photographic negative until photographic hardening of the exposed portions of the light-sensitive film is effected; the plate is then developed by washing with warm water, to remove the soluble portions of the film. Generally, a so-called "developing ink" is applied to the plate prior to the washing operation in order to insure that the insoluble portions, which define the image to be printed, will be receptive to the oily printing inks used.

Recently it has been proposed to replace the gelatine or albumen used heretofore as a basis for light-sensitive layers with polyvinyl alcohol. The latter material has the advantage that its properties can be controlled more precisely than those of natural products like gelatine and albumen; also polyvinyl alcohol films possess greater mechanical strength and durability than those formed from gelatine or albumen. However, certain difficulties have been encountered in the practical utilization of polyvinyl alcohol films in photolithographic plates, one of the most important of which is the fact that they tend to lose their properties of ink receptivity after relatively short periods of use. The loss of ink receptivity is especially pronounced when used polyvinyl alcohol plates are cleaned with solvents such as gasoline or turpentine. After such treatment it is usually impossible to restore the ink receptivity of the polyvinyl alcohol film.

It is, accordingly, an object of the present invention to provide improved light-sensitive compositions adapted to be used for the production of printing surfaces and for general photographic purposes. It is a further object of the invention to provide printing media characterized by a high degree of ink-receptivity, durability and resistance to the action of water and acids. Other objects will be apparent from the ensuing description of the invention.

The foregoing and related objects are accomplished by the incorporation of rubber or rubber-like materials in polyvinyl alcohol compositions utilized for preparing photographic plates and other printing and photographic media. I have found that films formed from such compositions possess an ink receptivity markedly superior to that of the usual polyvinyl alcohol films; that at the same time the new compositions have greater durability and resistance to the action of water, acids and "fountain solutions"; and that, in general, the modified polyvinyl alcohol compositions of the invention are superior to unmodified polyvinyl alcohol for practically all printing and photographic purposes.

In accordance with the invention, compositions suitable for preparing light-sensitive coatings on photolithographic and other printing surfaces and for the preparation of light-sensitive emulsions on photographic films and plates may be prepared by dissolving or dispersing rubber or rubber-like materials, preferably in the form of a latex, together with polyvinyl alcohol and a light-sensitizing agent, in water or other suitable solvent or dispersing medium. The resultant solutions or dispersions may be applied to a suitable support, for example, in the case of lithographic plates, to a zinc or aluminum plate, and the solvent removed by evaporation. The production of the image on the plate and its subsequent development and utilization in the printing process is effected in the same manner as

with the gelatine or albumen media used heretofore.

Polyvinyl alcohol is a water-soluble, resin-like material which is usually obtained by the hydrolysis of polymerized vinyl esters, such as polyvinyl acetate. Polyvinyl alcohol can be made in a number of modifications of different degrees of polymerization, the degree of polymerization depending largely upon the extent to which the polyvinyl compound from which it is derived has been polymerized. All of these modifications of polyvinyl alcohol are, to some extent, soluble in water. The more highly polymerized forms are less soluble and produce solutions of higher viscosities for equal concentrations than the lower polymers. There are also a number of the so-called partial derivatives of polyvinyl alcohol in which some of the hydroxyl groups in the molecule are replaced by other radicals, such as ester, ether or acetal radicals. Such partial derivatives may be produced by the incomplete saponification of vinyl esters or by the incomplete reaction of polyvinyl alcohol with acids, aldehydes or other compounds which react with hydroxyl groups. As would be expected, the properties of the partial derivatives of polyvinyl alcohol vary in accordance with the proportion of hydroxyl radicals that have been substituted for other groups. When the hydroxyl radicals substantially predominate, the partial derivatives show essentially the properties of polyvinyl alcohol and, like pure polyvinyl alcohol, are soluble in water as distinguished from the esters, acetals, etc., which are soluble only in organic solvents. Accordingly, the term "polyvinyl alcohol" is used herein and in the appended claims to designate generically all of the foregoing modifications of polyvinyl alcohol including such partial derivatives thereof as contain a sufficient number of unsubstituted hydroxyl groups as to render the compounds soluble in water.

As the viscosity of a solution of polyvinyl alcohol of given concentration is a function of its degree of polymerization, I refer herein to the various polymers in terms of viscosity. It is to be understood that all such references designate the viscosity of a 4% aqueous solution of the polyvinyl alcohol at a temperature of 20° C.

A wide range of polyvinyl alcohol polymers are adapted for use in the compositions of the present invention. Thus depending upon the particular purpose for which the compositions are to be used, polyvinyl alcohol polymers having a viscosity of from about 2 to about 60 centipoises may be used. In general, the lower polymers are more sensitive to slight differences in light intensity, but are somewhat less resistant to water than the higher polymers. The higher polymers form somewhat more durable printing surfaces. In certain cases it has been found desirable to utilize mixtures of high polymers and low polymers.

The rubber utilized for modifying the characteristics of the polyvinyl alcohol, in accordance with the invention may be any natural rubber or rubber-like material or synthetic rubber such as polymerized isoprene, polymerized butadiene, polymerized halogen substituted butadienes, e. g. 2-chlor-1,3-butadiene polymer or the like. Accordingly, the term "rubber", as used in the specification and claims, unless otherwise qualified, is intended to include all of the foregoing types of material.

Preferably the rubber is added to the polyvinyl alcohol solution in the form of a suspension or dispersion in order to ensure complete homogeneity of the composition. A convenient form of rubber dispersion is natural rubber latex, although synthetically prepared dispersions or latices may, of course, also be used. In case the rubber latex exhibits a tendency to coagulate in the presence of the polyvinyl alcohol, it is desirable to add a small amount of a stabilizing agent such as ammonia.

The amount of rubber utilized in the compositions may vary through rather wide limits, depending upon the purpose for which the composition is to be used and the result which it is desired to obtain. In general, the amount of rubber may range from about 1% to 50% of the weight of the polyvinyl alcohol contained in the composition and will generally be within the limits of 3% to 20%.

The agents used to render the compositions light-sensitive may be any of those which have been used heretofore for similar purposes in gelatine or albumen films. For the preparation of photolithographic plates and for similar printing purposes, the preferred sensitizing agents are soluble chromium salts, such as, for example, ammonium dichromate or alkali metal dichromates. For the preparation of photographic emulsions, silver salts, especially silver halides, light-sensitive dyes and other sensitizing agents such as are well known in the photographic art may be employed.

The following example is illustrative of a specific embodiment of the invention:

Example

One hundred grams of a 6% aqueous solution of polyvinyl alcohol (a polymer having a viscosity of 22–24 centipoises in 4% aqueous solution at 20° C.) was mixed with 1.6 grams of a natural rubber latex containing 38% (0.6 gram) of rubber. To the mixture was then added 1 cubic centimeter of 20% aqua ammonia and 100 cubic centimeters of 3% ammonium dichromate solution.

A zinc lithographic plate was coated with this solution, dried, and exposed to ultra-violet light under a photographic negative. The exposed plate was coated with developing ink and developed by washing with water at a temperature of 35 to 40° C. The developed print was then coated with the usual "gum solution" (an aqueous solution containing gum arabic with small amounts of phosphoric and gallic acids). The plate was then ready for use in the lithographic printing press.

The image on the plate thus prepared is uniformly receptive to the lithographic ink and retains such ink receptivity after long periods of use, even after having been washed with turpentine, gasoline or other solvents. The film possesses water-resistance superior to that of films made from unmodified polyvinyl alcohol. If desired, however, the water-resistance may be further increased by heating the developed plate, for example, to a temperature of 80–120° C. for a period of 5 minutes to one-half hour. Where extreme insolubility of the film is desired, vulcanizing agents, accelerators and the like, such as are commonly employed in the rubber art, may be incorporated in the compositions and the films formed therefrom vulcanized.

In certain instances the polyvinyl alcohol compositions of the invention can be combined with compositions used heretofore as a basis for light-sensitive films, such as albumen, gelatine,

glue, gum arabic and the like. For special applications, dyes, pigments and filling agents of various kinds may be added to the compositions.

While the invention has been described primarily from the standpoint of the production of improved photolithographic plates, it is to be understood that the utility of the compositions of the invention is not restricted to photolithography or similar process. They may be used advantageously in substantially all printing and photographic arts wherein gelatine or albumen compositions have been used heretofore. They are suitable for both positive and negative printing processes, whether the films be utilized as ink-receptive printing surfaces or as etching masks. The compositions may be used advantageously for coating paper or fabrics to produce carbon tissues such as are commonly utilized in intaglio printing and in certain types of photographic finishing. Another application of the compositions is in the photographic production of mesh stencils of the type where a photosensitive material is utilized as a mask for the non-design portions of the stencil. The compositions of the invention may also be utilized as emulsion coatings for photographic films and plates, both positive and negative.

Printing plates prepared from the compositions of the invention are characterized by improved qualities of ink receptivity and by the retention of such ink receptivity even after long continued use and after treatment with solvents. They are also considerably more resistant both to water and to acids than films prepared from unmodified polyvinyl alcohol and are characterized by greater durability and superior printing qualities.

It is to be understood that the invention is not restricted to any of the specific embodiments described hereinabove but includes all such variations, modifications and equivalents as fall within the scope of the appended claims.

I claim:

1. A composition comprising polyvinyl alcohol, dispersed rubber in an amount ranging from about 1% to 50% by weight of the polyvinyl alcohol and a light-sensitizing agent.

2. A composition comprising an aqueous dispersion of polyvinyl alcohol, rubber latex in an amount ranging from about 1% to 50% by weight of the polyvinyl alcohol and a light-sensitizing agent.

3. A composition comprising polyvinyl alcohol, dispersed rubber in an amount ranging from about 1% to about 50% by weight of the polyvinyl alcohol and a water-soluble chromic acid salt in light-sensitizing amount.

4. A composition comprising polyvinyl alcohol, dispersed rubber in an amount ranging from about 1% to about 50% by weight of the polyvinyl alcohol and a water-soluble dichromate in light-sensitizing amount.

5. A printing device having on its printing surface ink-receptive design portions, said ink-receptive portions comprising hardened polyvinyl alcohol, and dispersed rubber in amount sufficient to give said design portions a high ink-receptivity.

6. A light-sensitive layer comprising polyvinyl alcohol, dispersed rubber in amount sufficient to give the layer a high ink-receptivity and a light-sensitizing agent.

7. A light-sensitive layer comprising polyvinyl alcohol, dispersed rubber in amount sufficient to give the layer a high ink-receptivity, and a water-soluble chromic acid salt in light-sensitizing amount.

8. A light-sensitive layer comprising polyvinyl alcohol, dispersed rubber in amount sufficient to give said layer a high ink-receptivity, and a water-soluble dichromate in light-sensitizing amount.

9. An article, adapted for printing and photographic purposes when selectively exposed to light and developed, comprising a base having a light sensitive layer thereon containing polyvinyl alcohol and dispersed rubber in amount sufficient to give said layer a high ink-receptivity.

10. An article comprising a base having a light-sensitive layer thereon containing polyvinyl alcohol and dispersed rubber, the amount of rubber being about 1% to about 50% by weight of the polyvinyl alcohol.

11. A method of producing a photographic or printing device which comprises forming a film comprising polyvinyl alcohol, a light-sensitizing agent and dispersed rubber in amount sufficient to give said film a high ink-receptivity, and selectively exposing said film to light.

12. A method of producing a photographic or printing device which comprises forming a film comprising polyvinyl alcohol, a light-sensitizing agent and dispersed rubber in amount sufficient to give said film a high ink-receptivity, selectively exposing said film to light, and developing said film to remove non-exposed portions thereof.

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