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PHOTOGRAPHIC AND PRINTING MEDIA

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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 wth polyvinyl alcohol. The latter material has the advantage that its properties can be controlled more precisely than thoseof 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 polybasic carboxylic acids with the polyvinyl alcohol compositions utilized heretofore for preparing photolithographic plates and other printing and photographic media. We 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, polyvinyl alcohol-polybasic acid compositions 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 polyvinyl alcohol, polybasic carboxylic acid and a light-sensitizing agent in water or other suitable solvent. The resultant solutions 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 hy-

drolysis 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.

The acids suitable for modifying the characteristics of polyvinyl alcohol in accordance with the invention include all organic carboxylic acids containing two or more carboxyl groups. In the case of acids which are not normally watersoluble, it is advantageous to utilize them in the form of their water-soluble salts, e. g., as ammonium or alkali metal salts. Suitable polycarboxylic acids include: the saturated aliphatic polybasic acids such as oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, tricarballylic and mucic acids; hydroxy acids such as malic, citric, and saccaric acids; unsaturated acids such as maleic, fumaric, itaconic and citraconic acids; aromatic acids such as phthalic, terephthalic, mellitic, diphenic, naphthalene dicarboxylic and dihydronaphthalenedicarboxylic acids; heterocyclic polybasic acids such as quinolinic and cinchomeronic; polymeric acids such as polyacrylic and polymethacrylic acids and water soluble interpolymers of methyl methacrylate and methacrylic acid; celluloseglycollic acid; pectin and pectic acid; alginic acid; and water-soluble glyptals containing free carboxyl groups. The acids which are soluble in water may be incorporated directly with the polyvinyl alcohol solution; in the case of acids which are normally insoluble or only very slightly soluble in water, it is advantageous to convert them to a soluble salt, such as an ammonium or alkali metal salt, to enable them to be dissolved in the polyvinyl alcohol solution. If desired, the corresponding acid anhydrides may be used instead of the acids.

The amount of polybasic acid 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. Thus the amount of polybasic acid may range from 0.1% to 100% of the weight of the polyvinyl alcohol contained in the composition and will generally be within the limits of 0.2% to 50% of the weight of the polyvinyl alcohol. For photolithographic purposes, it is generally preferred to use an amount of polybasic acid equivalent to about 1% to 20% of the weight of polyvinyl alcohol.

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 examples are illustrative of certain specific embodiments of the invention:

Example I

A composition was prepared from the following ingredients:

	Parts by weight
Polyvinyl alcohol (A polymer having a viscosity of about 24 centipoises in 4% aqueous solution at 20° C.)	3.0
Maleic anhydride	0.5
Ammonium dichromate	1.5
Water	95.0

The polyvinyl alcohol was dissolved in 50 parts of water and, to this solution, was added the maleic anhydride. The mixture was then heated, with stirring, to a temperature of about 90° C. for a period of 2½ to 4 hours. After cooling to 70° C. the ammonium dichromate, dissolved in the remainder of the water, was added with stirring.

A zinc lithographic plate was coated with this solution, dried and exposed to ultra-violet light under a photographic negative. The exposed plate was then 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, vasoline 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 still further increased by heating the developed plate to a temperature of 80 to 120° C. for a period of 5 minutes to one-half hour.

Example II

	Parts by weight
Polyvinyl alcohol (Same polymer as in Example I)	3.0
Sebacic acid	0.3
Ammonium dichromate	1.5
Aqua ammonia (20% NH_3)	0.5
Water	95.0

The polyvinyl alcohol was dissolved in 50 parts of water. The sebacic acid was separately dissolved with the aqua ammonia in 20 parts of water and mixed with the ammonium dichromate dissolved in the remainder of the water. The resultant solution was then stirred into the polyvinyl alcohol solution and the composition was utilized for the preparation of lithographic plates in the same manner as in Example I.

As has been indicated above, the water-resistance of the compositions can be improved by heating the developed film to a temperature of about 80 to 120° C. In addition to, or instead of, this procedure the initial solutions of mixtures of the polyvinyl alcohol and the polybasic acid may be heated to a temperature on the order of 80 to 90° C. for several hours to cause partial reaction of the polyvinyl alcohol with the acid. Such treatment renders the compositions more readily insolubilized by subsequent heat treatment.

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 photo-lithography 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, 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.

We claim:

1. A light-sensitive layer comprising polyvinyl alcohol, a polybasic carboxylic acid in amount sufficient to give said layer a high ink receptivity and a light-sensitizing agent.

2. A light-sensitive layer comprising polyvinyl alcohol, a polybasic carboxylic acid in amount sufficient to give said layer a high ink receptivity and a water-soluble chromic acid salt in light-sensitizing amount.

3. A light-sensitive layer comprising polyvinyl alcohol, a polybasic carboxylic acid in amount sufficient to give said layer a high ink receptivity and a water-soluble dichromate in light-sensitizing amount.

4. An article comprising a base having a light-sensitive layer thereon containing polyvinyl alcohol, a light-sensitizing agent and a polybasic carboxylic acid in amount sufficient to give said layer a high ink receptivity.

5. An article comprising a base having a light-sensitive layer thereon containing polyvinyl alcohol, a light-sensitizing agent, and a polybasic carboxylic acid, the amount of polybasic carboxylic acid being about 1% to about 20% by weight of the polyvinyl alcohol.

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

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

8. A light-sensitive layer comprising polyvinyl alcohol, maleic acid in amount sufficient to give said layer a high ink-receptivity, and a light-sensitizing agent.

9. A light-sensitive layer comprising polyvinyl alcohol, sebacic acid in amount sufficient to give said layer a high ink-receptivity, and a light-sensitizing agent.

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