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PHOTOGRAPHIC COMPOSITIONS AND PHOTOGRAPHIC ELEMENTS

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This invention relates to photography and, more particularly, to novel compositions comprised of photosensitive material and certain synthetic resinous copolymers of olefinic hydrocarbons with copolymerizable dicarboxy compounds, which copolymers have both carboxylic ester and carboxylic acid groups. The compositions of this invention are particularly useful for coating a surface intended to receive a photographic reproduction of a latent or visual image. The invention includes photographic elements which are represented by a surface having a coating of one or more layers of a novel composition of this invention. The invention also embraces printing, developing, and fixing the images which are reproduced, using the novel compositions of this invention.

The term "photosensitive material," as used herein in the specification and claims, defines single chemical compounds or mixtures of chemical compounds which are chemically affected by the action of a part or all of the radiant energy in that portion of the electromagnetic spectrum between and including infrared and X-rays. Accordingly, the term "photographic" is used herein to define the reproduction of images by the action of such radiant energy upon photosensitive material.

In that portion of the graphic arts industry as represented by photography, photoengraving, photolithography, collotypy, etc., gelatin, albumin, polyvinyl alcohol, cellulose nitrate, and certain other natural and synthetic polymeric materials have been used, either alone or in some combination, as carriers for photosensitive materials in the preparation of a photosensitive layer of a photographic element. Because of the peculiar requirements of photographic reproduction processes, gelatin or albumin have remained as the principal carriers or binding agents for photosensitive materials in the photosensitive layers. Any undeveloped photosensitive coatings which contain these natural materials as the principal carriers, must be protected from moisture during use and are unstable at high or low temperatures, which limit their use in certain climates and require that costly packaging methods be used. Furthermore, developed and fixed photosensitive coatings in which these natural materials are the principal binding agents or carriers, have relatively poor abrasion-resistance and are susceptible to attack by biological organisms such as fungi. In addition, many of the coating solutions whether the carrier or binding agent be gelatin, albumin, polyvinyl acetate, polyvinyl alcohol, etc., contain relatively large quantities of water, necessitating a lengthy drying step to remove this water as a part of the procedure for forming a photosensitive layer on a base material.

An object of this invention is to provide new and useful photosensitive compositions which are stable, of little or no water content, and can be used to provide smooth, tough, abrasion-resistant, and tightly adherent photosensitive coatings on surfaces of glass, metal, films of synthetic resins, wood, paper, and the like. A further object is to provide photosensitive compositions which are

easily applied to such surfaces, fast drying, not softened by water or attacked by acid, and have good adherence to water-resistant and hard-to-coat surfaces. A further object is to provide photographic elements with water-insoluble photosensitive layers which are fast printing and can be processed rapidly in alkaline developing mediums to yield reproductions of high contrast, resolving power and definition.

The above objects are attained by the preparation and use of the novel compositions of this invention which are comprised of photosensitive material and resinous copolymer of olefinic hydrocarbon with alpha-, beta-ethylenically unsaturated dicarboxy compound, which copolymer has both carboxylic acid and certain carboxylic ester groups.

The novel photosensitive compositions of this invention lend themselves to simple and reproducible application procedures to surfaces of glass, metal, films of synthetic resins, and other commonly used film supports. After exposure, coatings of the photosensitive compositions of this invention can be swollen to allow penetration of processing solutions without permanent impairment of the strength, toughness, or permanence of the coating. Coatings of these compositions show minimum distortion during processing and use. A particular feature of the novel compositions of this invention is that the photographic elements prepared therefrom can be prepared to respond to photochemical and photomechanical development processes.

In the practice of this invention, resinous copolymers can be used where the olefinic hydrocarbon monomer is an aliphatic olefinic hydrocarbon or an aryl olefinic hydrocarbon. Aliphatic olefinic hydrocarbon monomers are, for example, ethylene, propylene, n- and iso-butylene, and higher homologous and isomeric olefins, such as the octenes, decenes, dodecenes, and octadecenes, as well as higher olefins prepared by the polymerization of shorter-chain olefins, such as the dimers, trimers, tetramers, and pentamers of propylenes and butylenes. Aryl olefinic hydrocarbon monomers are, for example, styrene, the o-, m- and p-methyl styrenes, the o-, n-, and p-ethyl styrenes, dimethyl styrene, alpha-methyl styrene, the vinyl naphthalenes, etc.

In the preparation of the resinous copolymer, the olefinic hydrocarbon monomer is copolymerized with an alpha-, beta-ethylenically unsaturated dicarboxy compound, such as maleic anhydride, maleic acid, fumaric acid, citraconic acid, itaconic acid, and half-esters (i.e., acid esters) of these acids and mixtures thereof.

It is required that the resinous copolymers to be used in the practice of our invention contain both carboxylic acid and certain carboxylic ester groups, with the further requirement that 5–9% of the total of these carboxy groups be particular carboxylic ester groups. Preferably, from about 10% to about 60% of the total of these carboxy groups are the carboxylic ester groups. The preparation of these resinous copolymers having both carboxylic acid and carboxylic ester groups in the required proportion, can be accomplished by a number of different methods. For example, the olefinic hydrocarbon can be first copolymerized with maleic anhydride and the resulting copolymer subjected to controlled partial esterification to yield a resinous copolymer having both carboxylic acid and carboxylic ester groups in the desired proportion. While this controlled partial esterification can be accomplished after the copolymer of the olefinic hydrocarbon and maleic anhydride has been completely prepared, there are techniques known to the art whereby the controlled partial esterification is carried out simultaneously with the step for the copolymerization of the olefinic hydrocarbon and maleic anhydride.

An alternative method is to copolymerize the olefinic hydrocarbon with a dicarboxy compound in which one of the carboxy groups is a carboxylic ester group such as a half-ester of maleic or fumaric acids. When this method is followed, it will be understood that, in the resulting resinous copolymer, half of the carboxy groups will be carboxylic acid groups and the other half of the carboxy groups will be carboxylic ester groups. Another alternative method is to copolymerize the olefinic hydrocarbon with alpha-, beta-unsaturated dicarboxy compound in which both of the carboxy groups are carboxylic ester groups, to produce a resinous copolymer in which substantially all of the carboxy groups present are carboxylic ester groups and thereafter subjecting this esterified copolymer to controlled partial hydrolysis so as to hydrolyze only a portion of the ester groups to yield a copolymer containing both carboxylic acid and carboxylic ester groups in the desired proportion. The final resinous copolymer containing both the carboxylic acid and the carboxylic ester groups in the desired proportion can contain a small portion of polymer units in which the carboxy groups have not been esterified. For example, when maleic anhydride is used as the copolymerizing monomer, the resulting resinous copolymer can contain copolymer units in which the maleic anhydride heterocycle is not broken or in which both of the carboxy groups are carboxylic acid groups even after the resinous copolymer, as a mass, has been subjected to controlled partial esterification.

The carboxylic ester groups which the resinous copolymers are required to contain for use in the practice of our invention are aliphatic ester groups, such as methyl, ethyl, n- and iso-propyl, m-, sec.-, and iso-butyl and other higher homologous and isomeric ester groups, such as 2-ethylhexyl, 2-butyloctyl, hexadecyl ester groups, as well as those ester groups which can be derived from "oxo" alcohols generally containing 7 to 17 carbon atoms; other suitable aliphatic ester groups are alkoxy-alkyl ester groups, such as methoxyethyl, 2-ethoxyethyl, and 2-butoxyethyl groups; unsaturated aliphatic ester groups are also suitable, such as allyl, methallyl, and propargyl ester groups; aromatic carboxylic ester groups are also suitable, such as the phenyl, phenethyl, phenylpropyl, methylphenylmethyl, and benzyl ester groups; cycloaliphatic carboxylic ester groups are also suitable, such as the cyclopentyl and cyclohexyl ester groups.

It will be clear from the foregoing and the numerous examples cited hereinafter that the term "carboxylic ester group" means the ester group formed by the esterification of the carboxyl group of the α,β-ethylenically unsaturated dicarboxylic acid with a monohydroxy compound of the above-listed illustrative materials, i.e. aliphatic alcohols, alkoxy alkanols, aromatic alcohols, and cycloaliphatic alcohols.

The resinous copolymers to be used in the practice of our invention should have a molecular weight of from about 1,000 to about 600,000. The preferred resinous copolymers are those having molecular weights within the range of from about 20,000 to about 300,000. As used herein, the molecular weight of a resinous copolymer is to be understood to mean the weight average molecular weight as determined by the Staudinger method.

In general, suitable resinous copolymers are prepared by polymerizing about one mol proportion of olefinic hydrocarbon with about one mol proportion of the alpha-, beta-ethylenically unsaturated dicarboxy compound. We find that maleic anhydride and the half-esters of maleic acid are preferred dicarboxy monomers for the preparation of the resinous copolymers to be used in the practice of our invention.

Specific examples of resinous copolymers which are representative of those suitable for use in the practice of our invention will be described briefly, however the

invention is not limited to the use of these specific resinous copolymers:

(1) Resinous copolymer having a molecular weight of about 120,000, prepared by the copolymerization of equal mol proportions of methyl styrene and maleic anhydride, which copolymer has been partially esterified so that about 20% of the carboxy groups are carboxylic acid groups and 80% of the carboxy groups are cyclohexyl carboxylic ester groups.

(2) Resinous copolymer having a molecular weight of about 70,000, prepared by the copolymerization of equal mol proportions of styrene and 2-ethylhexyl half-ester of maleic acid.

(3) Resinous copolymer having a molecular weight of about 20,000, prepared by the copolymerization of equal mol proportions of styrene and maleic anhydride, which copolymer has been partially esterified so that approximately 70% of the carboxy groups are carboxylic acid groups and 30% of the carboxy groups are benzyl carboxylic ester groups.

(4) Resinous copolymer having a molecular weight of about 25,000, prepared by the copolymerization of one mol of styrene with 0.5 mol of maleic anhydride and 0.5 mol of the butyl half-ester of maleic acid.

(5) Resinous copolymer having a molecular weight of about 200,000, prepared by the copolymerization of equal mol proportions of styrene and maleic anhydride, which copolymer has been partially esterified so that about 70% of the carboxy groups are carboxylic acid groups and 30% of the carboxy groups are carboxylic ester groups derived from a 50/50 mixture of allyl alcohol and methyl alcohol.

(6) Resinous copolymer having a molecular weight of about 30,000, prepared by the copolymerization of equal mol proportions of styrene with the half-ester of maleic acid, in which the ester groups are derived from "oxo" alcohols having 8 carbon atoms.

(7) Resinous copolymer having a molecular weight of about 20,000, prepared by copolymerizing one mol proportion of ethylene with about one mol proportion of maleic anhydride, which copolymer has been partially esterified with about 0.8 mol proportion of an "oxo" alcohol having 10 carbon atoms.

(8) Resinous copolymer having a molecular weight of about 80,000, prepared by copolymerizing one mol proportion of propylene with about one mol proportion of maleic anhydride, and subsequent partial esterification with about 0.4 mol proportion of cyclohexanol.

(9) Resinous copolymer having a molecular weight of about 140,000, prepared by the copolymerization of 0.5 mol proportion of propylene trimer (a 9-carbon monoolefin), 0.2 mol proportion of maleic anhydride, and 0.3 mol proportion of the tetradecyl half-ester of maleic anhydride.

(10) Resinous copolymer having a molecular weight of about 50,000, prepared by the copolymerization of equal mol proportions of styrene and maleic anhydride, and wherein, during the copolymerization, there is added about ⅛ mol proportion of methyl alcohol and ⅜ mol proportion of butyl alcohol.

(11) Resinous copolymer having a molecular weight of about 60,000, prepared by the copolymerization of equal mol proportions of styrene and maleic acid, which copolymer has been partially esterified with 0.6 mol proportion of butanol.

(12) Resinous copolymer having a molecular weight of about 40,000, prepared by the copolymerization of equal mol proportions of alpha-methyl styrene and dibutyl maleate, and subsequent hydrolysis to convert 20% of the butyl ester groups to carboxylic acid groups.

(13) Resinous copolymer having a molecular weight of about 90,000, prepared by the copolymerization of 0.5 mol proportion of styrene, 0.25 mol proportion of

maleic acid, and 0.25 mol proportion of di-2-ethylhexyl maleate.

(14) Resinous copolymer having a molecular weight of about 70,000, prepared by the copolymerization of equal mol proportions of dodecene and maleic acid, and subsequent esterification with one mol proportion of cyclohexanol.

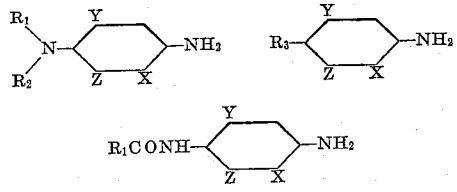
(15) Resinous copolymer having a molecular weight of about 20,000, prepared by the copolymerization of equal mol proportions of octene-1 and maleic acid, and subsequent partial esterification with 0.6 mol proportion of benzyl alcohol.

The resinous copolymers used in this invention may be prepared by various methods known to those skilled in the art of preparing synthetic resins by copolymerization of copolymerizable monomers. The copolymers can be prepared by reacting and polymerizing the olefinic hydrocarbon with suitable alpha-, beta-ethylenically unsaturated dicarboxy compounds by conventional polymerization methods, as for example, by heating, exposing to actinic light, or by the use of polymerization catalysts or any combination of these polymerization accelerators, in mass, in solution, or in suspension or in emulsion in water or a non-solvent. The copolymers so formed are then generally reacted with the selected alcohol or mixture of alcohols to partially esterify the available carboxy groups.

Photosensitive material useful in the novel composition of this invention, broadly speaking, include the light-sensitive diazo compounds such as those obtained by diazotization of asymmetric n-alkyl or aryl p-phenylene diamines, the anilides of dialkoxy phenylene diamines, the diazo-oxides and amides of such compounds, and others which are hereinafter described in greater detail; dichromates such as ammonium dichromate, potassium dichromate, etc.; iron systems such as mixtures of ammonium citrate and an alkali metal ferricyanide; iron-silver systems (Van Dyke) such as ferric ammonium citrate and silver nitrate; photosensitive salts of silver such as the chloride, bromide, iodide, phosphate, and acetate salts, other organic anions, or mixtures of these.

The compositions containing light-sensitive diazo material can be of the one-component type, wherein the diazo is present in the light-sensitive composition and the coupler is present in the developing bath, or of the two-component type, wherein both diazo and coupler are present in the light-sensitive composition.

The light-sensitive diazo compounds most commonly used include those prepared from the following amines:



wherein R_1 and R_2 are organic radicals, e.g., aliphatic hydrocarbon, aromatic hydrocarbon, heterocyclic, etc.; also, R_1 and R_2 together may form a saturated, unsaturated, or heterocyclic ring. R_3 may be the same as R_1, or may be

$$-SR_1, \quad -OR_1, \quad -NHCOOR_1, \quad -NHCONHR_1.$$

X and Y may be H, Cl, Br, alkyl, aryl, alkoxy, aryloxy, haloalkyl, etc. Z is a hydrogen, or together with X, may form a heterocyclic or aromatic ring. Specific compounds of this type include p-aminoacetanilide, p-aminobenzanilide, 4-amino-2,5-dimethoxyacetanilide, 4-amino-2,5-dichlorobenzanilide, 1-amino-4-acetamininaphthalene, 4-aminodiethylaniline, 4-aminodimethylaniline, 4-amino-2-methyldiethylaniline, N-(p-aminophenyl) morpholine, N-(4-amino-2,5-diethoxyphenyl) piperadine, 1-amino-4-dimethylaminonaphthalene, 4-aminodiphenyl, 4-amino-2,5-dimethoxyphenyl urea, 4-amino-2,5-dichlorophenyl urea, etc.

The coupling components suitable for use with the light-sensitive diazo compounds above, are in general, phenols and naphthols, typical of which are the following:

Di- and trihydric phenols, e.g., resorcinol, phlorglucinol
Alpha- and beta-naphthol
1-naphthol-3,8-disulfonic acid
1,8-dihydroxynaphthalene-3,6-disulfonic acid
2-naphthol-6,8-disulfonic acid
2-naphthol-3,6-disulfonic acid
2,3-dihydroxynaphthalene
2,3-dihydroxynaphthalene-6-sulfonic acid
Acetoacetanilide and its substitution products
Phenylmethylpyrazolone and its substitution products
Amides of 2-hydroxy-3-naphthoic acid, e.g., the anilide, 3-methylanilide, alpha-naphthylamide, beta-naphthylamide, and 4-phenylanilide

Although aromatic amino coupling components cannot be added to the light-sensitive solutions since they react to form dyes even in acidic solution, they may be employed in the developer solution. Such compounds are aniline, naphthylamines, aminophenols, and aminonaphthols, unsubstituted or having substituents in the ring or in the amino group, e.g., o-toluene n-aminophenol, 1-amino-8-naphthol-3,6-disulfonic acid, etc.

There can be added to the compositions containing light-sensitive diazo compounds, various stabilizers such as urea, thiourea, allylthiourea, inorganic acids as boric, fluoroboric, inorganic salts as zinc chloride, and salts of organic acids such as tin, zinc, or cadmium salts of weak organic acids as tartaric, citric, succinic, etc. Pigments, opaifiers, and flatteners, such as titanium dioxide, alumina, silica, etc., can be employed in the compositions of this invention to improve contrast or to change texture.

Compounds which prevent decomposition of the light-sensitive diazonium compounds when coated on metal plates are, for example, corrosion inhibitors and metal deactivators, such as tricresyl phosphate, didodecyl phosphate, sodium nitrate, and amyl nitrate, etc. These compounds can be added in small amounts, i.e., from 0.01% to 0.2% by weight of the resin used.

When systems other than those employing diazo compounds, such as those involving silver halides, are used, modifying adjuvants, such as dyes which modify the optical sensitivity of silver halide, e.g., the cyanine dyes, including carbocyanine, merocyanine, neocyanine, etc., other dyes, antifogging agents, pigments, and the like, can be added.

If desired, plasticizers can be incorporated into the photosensitive compositions to increase the flexibility of the photosensitive composition when used as a film applied to a supporting surface. The incorporation of a plasticizer is particularly important when it is desired to make the photosensitive composition into the form of a free film. Flexible or pliable free films of the photosensitive compositions of this invention are particularly useful in cartographic work where it is frequently necessary to stretch or otherwise distort the film (as after a visible image has been developed) to bring the image into register with the master chart. Also, where plates having relief images are being prepared for multicolor printing, stretchability of the supporting base and the relief image are desirable to bring the plates into register for the successive printing of the different colors. Suitable plasticizers include the phthalate esters, for example, di-2-ethylhexyl phthalate, dimethyl phthalate, dimethylcellosolve phthalate, as well as other plasticizing esters such as methyl phthalyl ethyl glycolate, dimethyl adipate, dibutyl sebacate; and also glycols and glycol ethers such as ethylene glycol, hexamethylene glycol, polyethylene glycols, etc. In general, amounts of plasticizer up to about

50% by weight based on the total resin content of the composition can be used.

Other resins (natural or synthetic) can be incorporated into the photosensitive compositions to increase the water-insolubility of the compositions. These resins most desirably are hydrophobic in character and compatible with the particular copolymer selected from those herein described. Such additional resins are, for example, nitrocellulose, cellulose acetate, polyvinyl acetate, methylcellulose, etc. These resins can be used in amounts up to one part of the compatible resin per one part of a described resinous copolymer.

Cross-linking agents can also be added to the photosensitive composition or to the developing solution, in which case the desired degree of insolubilization is generally obtained by subjecting the photographic element to radiant heat. Cross-linking agents which react with the carboxyl groups of the resinous copolymers to produce insoluble clear films are, for example, formaldehyde, polyfunctional hydroxy or amino compounds such as ethylene diamine, ethanolamine, polyglycols, polyvinyl alcohol, etc.

The photosensitive compositions of this invention are particularly useful for coating a surface intended to receive a photographic reproduction of a latent or visual image. These photosensitive compositions are most conveniently applied to such surfaces as solutions of the photosensitive composition in a mutual solvent. The term "mutual solvent," as used herein, means a solvent or solvent mixture which will dissolve the other components of the photosensitive coating composition. The novel photosensitive layers or photographic elements produced therefrom by the complete or substantial removal of the mutual solvent during the coating operation, comprise a stratum which is composed essentially of the herein-described partially esterified resinous copolymer and photosensitive material. Since organic solvents may be used, the drying time normally necessary with photosensitive coatings can be greatly reduced. However, a small amount of water may be present in the solvent mixture to aid in dissolving certain of the photosensitive materials used.

The coating solutions can be prepared by dissolving the resinous copolymer and photosensitive material in a mutual solvent. As exemplary of mutual solvents which may be used in one or more of the combinations of this invention are: Esters such as methyl acetate, ethyl acetate, ethyl proprionate, ethyl butyrate, ethylglycolate, etc.; alcohols such as ethanol, iso-propanol, n-butanol, sec.-butanol, etc.; ketones such as acetone, methylethyl ketone, cyclohexanone, etc.

Where water is required to dissolve the photosensitive component, solvents or solvent solutions which are water-miscible to the extent of 10% or more of water, are preferred. Further, it is usually desirable to use organic solvents which have an appreciable vapor pressure at normal temperatures, so that drying times will be as short as possible.

The resinous ester and the photosensitive material can be dissolved separately in the same solution, or dissolved in different portions of the same solvent, or in separate miscible solvents, as, for example, dissolving the photosensitive material in water and the resinous ester in acetone and mixing the two solutions. Other constituents commonly employed with certain photosensitive materials can be added in like manner. The resulting solutions may then be applied to a support and the resulting layers dried. It should be noted that, in the preparation of the solutions and in the coating operations, radiations which will affect the photosensitive material used must be excluded.

Coating compositions which are comprised of photosensitive material, the described resinous copolymer and a mutual solvent, for ease of application, should be prepared so as to have a solids content (i.e., photosensitive material plus the resinous copolymer) of between 1% and 20%. However, we have found that the more suitable coatings are those solutions having such a solids content within the range of 7–10%, depending upon the particular resin employed and the method of application. Any of the conventional methods of coating or application may be used to apply coatings of the photosensitive composition, such as brushing, dipping, roller coating, or spraying. For spraying it is usually desirable to use a dilute solution containing a high percentage of a volatile solvent, while for dipping and brushing, higher solids content may be employed. Furthermore, for roller coating or doctor-knife coating, still higher solids content compositions may be employed. The advantageous properties of the photosensitive compositions of this invention are generally realized when the ratio of photosensitive material to resin is in the range of 1:2 to 1:40 parts by weight.

The photosensitive coating compositions of this invention have the advantages that they are easily prepared and can be applied by any of these conventional application procedures to any water-resistant surface, such as polyester glass cloth (a glass fiber polyester laminate having a thickness of about 5 mils, generally made by impregnating a single or multiple ply web of woven or non-woven glass fiber with a thermosetting polyester resin, such as polymerized styrenated diethylene glycol maleate), glass, metals such as aluminum, zinc, copper, carbon steel, stainless steel, iron, magnesium, or plastic films such as cellulose acetate, cellulose propionate, cellulose nitrate, cellulose acetate-butyrate, polyethylene terephthalate (sold under the trademark Mylar by Du Pont de Nemours), as well as to other conventional surfaces, such as paper, wood, composition board, etc. The coatings of these photosensitive compositions are smooth, tough, and water- and acid-resistant. Accordingly, the careful handling procedures which the graphic arts industry has been forced to follow in the past, can now be virtually eliminated by the use of the photosensitive coatings of this invention.

The speed at which the coating dries is naturally dependent on the solvent used, the concentration of the solution, and the application method. When the spray method is used, the coating dries almost instantaneously; when other methods are used, drying may be facilitated by passing a current of hot air over the surface.

The compositions of this invention have a wide utility and are generally useful in the graphic arts, wherein a reproduction of a drawing, design, plan, etc., is desired. Thus, in the manufacture of templates for use in preparing parts of airplanes, automobiles, boats, radio and electrical equipment, etc., the materials to be used, such as steel, aluminum, etc., are coated with the light-sensitive compositions of this invention, dried, exposed through the master drawing, and developed. The finished print is an exact reproduction of the original and adheres firmly to the metal or other material. Stencils or lettered transparencies may also be used to reproduce directions, identification numbers, etc., on parts or finished articles of manufacture. The photosensitive film elements of the present invention may also be used as print stock in the production of black and white prints.

A particular feature of some of the novel compositions of this invention is that the photographic elements prepared therefrom can be used for both photochemical and photomechanical methods of reproduction. Thus, not only those compositions containing ammonium or alkali metal bichromates as the light-sensitive material, but also those containing diazo compounds, can be used to obtain mechanical images, by rendering the composition insoluble or altering its surface in proportion to the exposure to light. Such photographic elements can be prepared solely by exposure to visible radiation, or to combinations of simultaneous or sequential exposure to visible and infra-red radiation. The images so produced

can be rendered visible or texturally distinguishable by development in an aqueous alkaline solution, and then rinsed in water to effect differential swelling or solution of the image and non-image areas. Alternatively, development may be accomplished by treatment with a solution containing a solvent for the unchanged resin, producing differential swelling or solution as above. These compositions, which are susceptible to photomechanical reproduction, are useful as the photosensitive coating in preparing resist images on printing supports, such as aluminum, zinc, copper, and magnesium, various alloys thereof, and non-metallic supports such as paper, cloth, or plastics. When these coatings on such supports are exposed to the actinic radiations to which the particular coating is responsive, the coating is rendered insoluble in proportion to the action of light thereon, and an image is developable therein. In general, the areas receiving the most actinic radiation are insolubilized relative to those receiving less exposure, and remain on the support when the coating is treated with solvents for the lesser exposed portions of the coating, leaving uncoated areas permitting subsequent etching, dyeing, or other treatment of the exposed substrate. The resulting plates can be used in the appropriate intaglio, planographic, or relief printing processes.

Further details of the practice of this invention are set forth with respect to the following specific examples, in which all parts are by weight unless specified otherwise:

Example 1

Two solutions are prepared as follows:

(A)	Parts
Methylethyl ketone	950
Resinous copolymer having a molecular weight of about 20,000, prepared by the copolymerization of equal mol proportions of styrene and maleic anhydride and esterifying 18% of the available carboxy groups with 0.36 mol proportion of methyl alcohol	110
Di-2-ethylhexyl phthalate	12

(B)	
Methylethyl ketone	450
p-Diethylaminobenzene diazonium fluoroborate	15

A light-sensitive coating solution is prepared by mixing 5 volumes of solution (A) with one volume of solution (B), and then diluting with 6 additional volumes of methylethyl ketone to obtain a sprayable solution. A photographic element is then prepared by spray coating an 8" x 10" polyester glass cloth sheet twice with this photosensitive solution, the first coating being permitted to dry before the application of the second coat. A cellulose acetate positive test sheet containing lines, numerals, and Ben Day in five different reductions is placed in contact with the photosensitive coating and placed thirty inches from an uncoated carbon arc lamp, and then exposed for one minute. A developing solution is prepared from one part of resorcinol, 5 parts of sodium carbonate, and 200 parts of water, and the exposed coated glass cloth is immersed in this developing solution for a period of one minute, followed by a water wash and immersion in a 5% acetic acid solution. A sharp, brown image is thereby produced upon the coated surface of the polyester glass cloth, which is a positive reproduction of the lines, numerals, and Ben Day of the test sheet. The surface bearing the image is smooth, hard, and mar-resistant.

Example 2

Two solutions are prepared as follows:

(C)	Parts
Methylethyl ketone	950
Resinous copolymer prepared by the copolymerization of equal mol proportions of styrene and half-ester of maleic acid, which copolymer has a molecular weight of about 50,000, and wherein ¾ of the ester groups are derived from butanol and the other ¼ from methanol	110
Di-2-ethylhexyl phthalate	12

(D)	
Zinc chloride double salt of 3-chloro-4-diethylaminobenzene diazonium chloride	15
30% phosphorous acid (sp. gr. 1.12)	33
Water	60
Acetone	380

A sprayable solution is obtained by mixing five volumes of solution (C) with one volume of solution (D).

An 8" x 10" polyester glass cloth is spray coated with the above photosensitive composition, exposed, developed, and fixed as in Example 1. The reproduction so obtained is an orange image of good gradation and clarity.

Example 3

The following solution is prepared:

(E)	Parts
2-methyl-4-diethylaminobenzene diazonium fluoroborate	15
Methylethyl ketone	450

One volume of solution (E) is mixed with five volumes of solution (C). The composition is then spray coated on an 8" x 10" polyester glass cloth sheet, dried and contact exposed with a test sheet in sunlight until visual bleaching occurs in the non-image areas (30 seconds in strong sunlight). The film is then immersed in a developing solution composed of one part of phloroglucinol, 5 parts of sodium carbonate, 20 parts of acetone, and 250 parts of water, for a period of one minute. The film is then dipped in a 5% acetic acid solution, washed thoroughly with water, and wiped dry. There is obtained a clear positive reproduction of the test sheet.

Example 4

A solution is prepared as follows:

(F)	Parts
4-N-phenylaminobenzene diazonium fluoroborate	15
Methylethyl ketone	450

One volume of solution (F) is added to 5 volumes of solution (C). This composition is then sprayed on a glass cloth sheet and exposed as in Example 3. The sheet is then immersed in a developing solution containing one part of 2,4-diaminotoluene, 20 parts of acetone, and 250 parts of water, for a period of one minute. The print is then processed as in Example 3. Prints made from supports sensitized as above show purple images with good sharpness and contrast.

Example 5

The photosensitive composition of Example 1 is sprayed on a supporting surface of each of the following materials: Glass, aluminum, and Mylar polyethylene terephthalate. The photosensitive elements so prepared are then exposed, developed, and fixed as in Example 1, yielding a clear, sharp reproduction of the test sheet lines and numerals. The coating is smooth and uniform and exhibits good adhesion, dry and wet.

Example 6

Employing the procedure of Example 1, except by substituting an equivalent amount of the copolymers listed below for the styrene-maleic anhydride copolymer of Example 1, clear positive reproductions are obtained.

(1) Resinous copolymer having a molecular weight of about 30,000, prepared by the copolymerization of equal mol proportions of ethylene and maleic anhydride and subsequent partial esterification with 0.8 mol proportion of 2-ethylhexanol.

(2) Resinous copolymer having a molecular weight of about 50,000, prepared by the copolymerization of equal mol proportions of propylene and maleic anhydride, and wherein, during the copolymerization, there is added one mol proportion of cyclohexanol, whereby about 50% of the carboxy groups in such copolymer are converted to cyclohexyl carboxylic ester groups.

(3) Resinous copolymer having a molecular weight of about 10,000, prepared by the copolymerization of equal mol proportions of alpha-methyl styrene and maleic acid, which copolymer has been esterified with 0.5 mol proportion of benzyl alcohol.

(4) Resinous copolymer having a molecular weight of about 60,000, prepared by the copolymerization of equal mol proportions of styrene and maleic acid, which copolymer has been partially esterified with 1.6 mol proportion of n-butanol, whereby 80% of the total of the carboxy groups are converted to butyl carboxylic ester groups.

(5) Resinous copolymer having a molecular weight of about 100,000, prepared by the copolymerization of equal mol proportions of 3,4-dimethyl styrene and dimethyl maleate, and subsequent hydrolysis to convert 50% of the methyl ester groups to carboxylic acid groups.

(6) Resinous copolymer having a molecular weight of about 30,000, prepared by the copolymerization of 0.5 mol proportion of styrene, 0.25 mol proportion of maleic acid, and 0.25 mol proportion of dicyclohexyl maleate.

(7) Resinous copolymer having a molecular weight of about 70,000, prepared by the copolymerization of equal mol proportions of styrene and maleic anhydride, which copolymer has been partially esterfield with 0.75 mol proportion of an "oxo" alcohol having 8 carbon atoms.

(8) Resinous copolymer having a molecular weight of about 25,000, prepared by the copolymerization of equal mol proportions of styrene and the benzyl half-ester of maleic acid.

(9) Resinous copolymer having a molecular weight of about 90,000, prepared by the copolymerization of equal mol proportions of styrene and the cyclohexyl half-ester of maleic acid.

(10) Resinous copolymer having a molecular weight of about 50,000, prepared by the copolymerization of equal mol proportions of p-ethyl styrene and maleic acid, and subsequent partial esterification with 0.8 mol of benzyl alcohol, whereby 40% of the total of the carboxy groups present are converted to benzyl ester groups.

(11) Resinous copolymer having a molecular weight of about 20,000, prepared by the copolymerization of 0.5 mol proportion of ethylene and 0.5 mol proportion of the dodecyl half-ester of maleic acid.

(12) Resinous copolymer having a molecular weight of about 80,000, prepared by the copolymerization of 0.5 mol proportion of propylene, 0.25 mol proportion of maleic acid, and 0.25 mol proportion of the iso-decyl half-ester of maleic acid.

(13) Resinous copolymer having a molecular weight of about 70,000, prepared by the copolymerization of equal mol proportions of iso-butylene and maleic acid, which copolymer has been esterified with one mol proportion of cyclohexanol, whereby 50% of the total carboxy groups are converted to cyclohexyl ester groups.

(14) Resinous copolymer having a molecular weight of about 200,000, prepared by the copolymerization of equal mol proportions of ethylene and the benzyl half-ester of maleic acid.

Example 7

A solution of the following composition is prepared:

	Parts
Methylethyl ketone	180
Resinous copolymer having a molecular weight of about 200,000, prepared by the copolymerization of equal mol proportions of styrene and maleic anhydride in the presence of 0.36 mol methanol so that 18% of the total carboxy groups in the polymer are present as carboxymethyl groups	20
p-Diethylaminobenzene diazonium fluoborate	1

The solution is flow-coated on polyester glass cloth sheet, hung in a vertical position to drain briefly, and drying is assisted with a blast of air. About 1.5 g. per 80 sq. in. of dry coating is thus deposited. The coated film is exposed behind a cellulose acetate test positive bearing lines, numerals, solids, and Ben Day in five different reductions, at a distance of thirty inches from a carbon arc lamp for one minute. The exposed film is immersed for one minute in a developing solution composed of resorcinol, 1 part; methyl phloroglucinol, 1 part; sodium carbonate, 5 parts; water, 200 parts; and alcohol, 20 parts. The film is then immersed briefly in a 5% acetic acid solution, rinsed in water, and dried. A sharp, dark-brown image is thereby produced within the coating on the polyester glass cloth which is a positive reproduction of the images on the test sheet.

Example 8

A solution is prepared as follows:

	Parts
Methylethyl ketone	180
Resinous copolymer of Example 2	20
Zinc chloride double salt of 3-chloro-4-dimethylaminobenzene diazonium chloride	1
Water	5

The solution is coated on polyester glass cloth using a Boston-Bradley doctor blade at a setting of 0.009 inch. The film is allowed to dry in a horizontal position and is then exposed and developed as in Example 7. The reproduction so obtained has a deep orange image of good contrast.

Example 9

A solution is prepared as follows:

	Parts
Methylethyl ketone	180
Resinous copolymer prepared by the copolymerization of equal mol proportions of ethylene and maleic anhydride, which copolymer has a molecular weight of about 4,000 and has been esterified with one mol proportion of n-octyl alcohol so that approximately 50% of the total carboxy groups are n-octyl carboxylic ester groups	20
2-methyl-4-diethylaminobenzene diazonium fluoborate	1

A polyester glass cloth sheet is coated, dried, exposed, and developed as in Example 7. A red-brown image is obtained.

Example 10

A solution is prepared as follows:

	Parts
Methylethyl ketone	180
The resinous copolymer of Example 2	20
p-Diethylaminobenzene diazonium fluoborate	1
Triaminotoluene trihydrochloride	0.5

The solution is flow-coated on polyester glass cloth and allowed to dry, then exposed under a positive to sunlight for one minute. The film is exposed to moist ammonia vapor by holding it over a bottle of concentrated aqueous

ammonia. A sharp, dark red-brown image appears immediately.

Example 11

Three solutions are prepared as follows:

	Parts
(1) Methylethyl ketone	180
Resinous copolymer of Example 2	20
(2) Ammonium bromide	1
Ethanol	10
(3) Silver nitrate	1
Water	2
Ethanol	7

Twenty volumes of solution 1, one volume of solution 2, and ½ volume of solution 3 are mixed. The resulting solution is flow-coated on polyester glass cloth, dried in a vertical position, and exposed to sunlight for 10 seconds under a photographic negative. A deep grey-black image is obtained by development in a developing solution composed of diamino phenol dihydrochloride (Amidol), 7 parts; sodium sulfite, 58 parts; potassium bromide, 1.5 parts; water, 950 parts.

Example 12

Two solutions are prepared as follows:

	Parts
(1) Methylethyl ketone	180
The resinous copolymer of Example 2	20
(2) Anhydrous ferric chloride	1
Acetone	10

Twenty volumes of solvent 1 are mixed with one volume of solution 2, and a sheet of polyester glass cloth is then coated with the mixture and dried. The film is exposed under a positive to sunlight for two minutes, then developed in a 10% solution of potassium ferricyanide in water. A white image on a deep blue background is produced.

Example 13

The procedure of Example 12 is repeated, except that a 20% solution of potassium ferrocyanide is substituted for the potassium ferricyanide. A dark blue image on a light blue background is produced.

Example 14

One part (by volume) of a 7½% aqueous alcohol solution (50/50 mixture of ethyl alcohol and water) of ammonium dichromate is added to a 10% solution of the resin of Example 2 in methylethyl ketone (containing a small amount of an alcohol soluble nigrosine dye). The resulting solution is spray coated on an 8" x 10" polyester glass cloth sheet. The sensitized element is then contact-printed through a negative using a carbon arc lamp and an exposure of three minutes. The unexposed area is easily removed by immersion in a 1:1 acetone:water solution, leaving a relief image in the exposed areas of excellent definition and high durability.

Example 15

Substituting an equivalent amount of each of the copolymers of Example 6 for the resin of Example 2, the preceding experiment is repeated. The resulting relief image in each case in an excellent reproduction of the negative image which can be used in the same manner as bichromate-gelatin sensitized plates in photographic reproduction processes.

Example 16

An 8" x 10" sheet of Mylar, coated with the photosensitive composition of Example 2, is exposed, in contact with a positive transparent test sheet, with a shield to give 2, 4, 6, 8 , and 10 minute areas of exposure to a carbon arc lamp (30 inches from the film). The film is then exposed to a chromalox infrared heater (distance=8–10 inches) for a period of ten minutes. When the film is immersed in a 0.5% caustic developing bath, marked differential solubility is experienced, in that the image area washes out, while the non-image area remains intact.

Example 17

A solution is prepared as follows:

	Parts
Methylethyl ketone	180
The resinous copolymer of Example 2	20
p-Diethylaminobenzene diazonium fluoborate	1

The solution is flow-coated on polyester glass cloth, drained, and dried in a vertical position, exposed under a positive obtained by inking designs on a sheet of polyester glass cloth with india ink, to sunlight for one minute, then under a heat lamp for two minutes at a distance of 9 inches. The film is then developed in the developing solution of Example 1 and dipped for 10 seconds in an ammonia solution containing one volume of concentrated (28%) aqueous ammonium hydroxide and ten volumes of distilled water. The film is then rinsed in water. The image (colored) areas of the print swell more strongly than the non-image areas and can be rubbed or washed away. The dried print presents an intaglio reproduction of the positive.

Example 18

The procedure of Example 17 is repeated, except that exposure to the heat lamp is omitted. The non-image areas swell and an intaglio image is obtained.

Example 19

A solution is prepared as follows:

	Parts
Methylethyl ketone	180
The resinous copolymer of Example 8	20

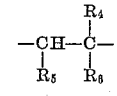
The solution is flow-coated on polyester glass cloth and hung vertically to drain and dry. The coated film is then exposed under a cut-out of opaque black paper at a distance of five inches from a heat lamp for three minutes. The film is dipped for ten seconds in a developing bath composed of one volume of concentrated (28%) aqueous ammonium hydroxide and ten volumes of distilled water, and is then rinsed in running water. The areas of the coating that were not under the black paper cut-out swell strongly and are washed away. The areas under the cut-out suffer little or no swelling, and preserve the image of the cut-out as relief area of insoluble coating.

After developing and fixing the coatings of photosensitive compositions of this invention, these coatings are characterized by insolubility in neutral or acidic aqueous solution, i.e., pH of 7 or less, however these coatings become progressively more soluble in aqueous alkaline solutions with increasing pH above 7. Generally, this solubility ranges from very slight at a pH slightly above 7 to ready and complete solubility at a pH of about 13. This solubility in aqueous alkaline solutions can be reduced in a number of ways, such as by adding significant amounts of a compatible hydrophobic resin or by post-heating (as by exposure to radiant heat) the developed and fixed coating. The addition of cross-linking agents, as previously described, increases even more the alkali-resistance of the coating upon post-heating the developed and fixed coating.

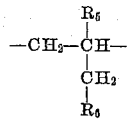
What is claimed is:

1. A photographic composition consisting essentially of a photosensitive material incorporated in a water-insoluble resinous copolymer; said photosensitive material being selected from the group consisting of light-sensitive diazo compounds, dichromates, iron systems, iron-silver systems, silver salts and mixtures thereof; said resinous copolymer containing in its formula both (*a*) polymerized olefinic hydrocarbon groups and (*b*) at least one poly-

merized monomer group having a formula of the group consisting of:



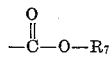
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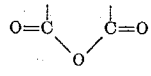
where R_4 is selected from the group consisting of a hydrogen atom and a methyl group and where R_5 and R_6 are independently selected from the group consisting of carboxyl groups of the formula:



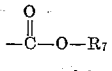
ester groups of the formula:



where R_7 is selected from the group consisting of alkyl groups, alkoxyalkyl groups, alkenyl groups, alkinyl groups, cycloalkyl groups and aryl groups, and an anhydride group of the formula:



formed by R_5 and R_6 collectively, with the further provision that 5–90% of the R_5 and R_6 groups are ester groups of the formula:



2. A photographic composition consisting essentially of a photosensitive material incorporated in a water-insoluble resinous copolymer; said photosensitive material being selected from the group consisting of light-sensitive diazo compounds, dichromates, iron systems, iron-silver systems, silver salts and mixtures thereof; said resinous copolymer being a copolymer of (*a*) an olefinic hydrocarbon and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.6 molar proportion, per molar proportion of maleic anhydride, of an alcohol selected from the group consisting of aliphatic alcohols, aromatic alcohols, and cycloaliphatic alcohols.

3. A photographic composition consisting essentially of a photosensitive material incorporated in a water-insoluble resinous copolymer; said photosensitive material being selected from the group consisting of light-sensitive diazo compounds, dichromates, iron systems, iron-silver systems, silver salts and mixtures thereof; said resinous copolymer being a copolymer of (*a*) styrene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.6 molar proportion, per molar proportion of maleic anhydride, of an alkanol containing 1–8 carbon atoms in its structure.

4. A photographic composition consisting essentially of a light-sensitive diazo compound incorporated in a water-insoluble resinous copolymer; said resinous copolymer being a copolymer of (*a*) styrene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.6 molar proportion, per molar proportion of maleic anhydride, of an alkanol containing 1–8 carbon atoms in its structure.

5. A composition consisting essentially of a light-sensitive diazo compound and a water-insoluble resinous copolymer dissolved in a mutual organic solvent; said resinous copolymer being a copolymer of (*a*) styrene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.6 molar porportion, per molar proportion of

maleic anhydride, of an alkanol containing 1–8 carbon atoms in its structure.

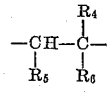
6. A photographic composition consisting essentially of a light-sensitive diazo compound incorporated in a water-insoluble resinous copolymer; said resinous copolymer being a copolymer of (*a*) styrene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.15 molar proportion, per molar proportion of maleic anhydride, of methanol and 0.35–0.45 molar proportion, per molar proportion of maleic anhydride, of butanol.

7. A composition consisting essentially of a light-sensitive diazo compound and a water-insoluble resinous copolymer dissolved in a mutual organic solvent; said resinous copolymer being a copolymer of (*a*) styrene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.15 molar proportion, per molar proportion of maleic anhydride, of methanol and 0.35–0.45 molar proportion, per molar proportion of maleic anhydride of butanol.

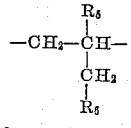
8. A photographic composition consisting essentially of a light-sensitive dichromate compound incorporated in a water-insoluble resinous copolymer; said resinous copolymer being a copolymer of (*a*) styrene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.6 molar proportion, per molar proportion of maleic anhydride, of an alkanol containing 1–8 carbon atoms in its structure.

9. A composition consisting essentially of a light-sensitive dichromate compound and a water-insoluble resinous copolymer dissolved in a mutual organic solvent; said resinous copolymer being a copolymer of (*a*) styrene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.6 molar proportion, per molar proportion of maleic anhydride, of an alkanol containing 1–8 carbon atoms in its structure.

10. A photographic composition consisting essentially of a photosensitive material incorporated in a water-insoluble resinous copolymer; said photosensitive material being selected from the group consisting of light-sensitive diazo compounds, dichromates, iron systems, iron-silver systems, silver salts and mixtures thereof; said resinous copolymer containing in its formula both (*a*) polymerized olefinic hydrocarbon groups, and (*b*) at least one polymerized monomer group having a formula of the group consisting of:



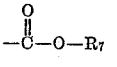
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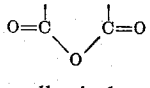
where R_4 is selected from the group consisting of a hydrogen atom and a methyl group and where R_5 and R_6 are independently selected from the group consisting of carboxyl groups of the formula:



ester groups of the formula:

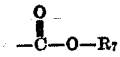


where R_7 is selected from the group consisting of alkyl groups, alkoxyalkyl groups, alkenyl groups, alkinyl groups, cycloalkyl groups and aryl groups, and an anhydride group of the formula:



formed by R_5 and R_6 collectively, with the further provi-

sion that 10–60% of the R_5 and R_6 groups are ester groups of the formula:



11. A photographic composition consisting essentially of a photosensitive material incorporated in a water-insoluble resinous copolymer; said photosensitive material being selected from the group consisting of light-sensitive diazo compounds, dichromates, iron systems, iron-silver systems, silver salts and mixtures thereof; said resinous copolymer being a copolymer of (*a*) ethylene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.6 molar proportion, per molar proportion of maleic anhydride, of an alkanol containing 1–12 carbon atoms in its structure.

12. A photographic composition consisting essentially of a light-sensitive diazo compound incorporated in a water-insoluble resinous copolymer; said resinous copolymer being a copolymer of (*a*) ethylene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.6 molar proportion, per molar proportion of maleic anhydride, of an alkanol containing 1–12 carbon atoms in its structure.

13. A composition consisting essentially of a light-sensitive diazo compound and a water-insoluble resinous copolymer dissolved in a mutual organic solvent; said resinous copolymer being a copolymer of (*a*) ethylene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.6 molar proportion, per molar proportion of maleic anhydride, of an alkanol containing 1–12 carbon atoms in its structure.

14. A photographic element comprising a surface bearing at least one layer of the photosensitive composition of claim 1.

15. A photographic element comprising a surface bearing at least one layer of the photosensitive composition of claim 4.

16. A photographic element comprising a surface bearing at least one layer of the photosensitive composition of claim 6.

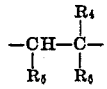
17. A photographic element comprising a surface bearing at least one layer of the photosensitive composition of claim 12.

18. A photographic element comprising a glass fiber reinforced polyester laminate bearing at least one outer lamina of the photosensitive composition of claim 1.

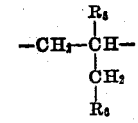
19. A photographic element comprising a metal surface bearing at least one layer of the photosensitive composition of claim 1.

20. A photographic element comprising a polyethylene terephthalate surface bearing at least one layer of the composition of claim 1.

21. The method of forming a relief image which comprises: (1) preparing a coated surface by coating a surface with a photographic composition consisting essentially of a photosensitive material incorporated in a water-insoluble resinous copolymer, (2) exposing the coated surface to light with a replica of the relief image interposed between the light source and the coated surface, and (3) treating the coated surface with a solution to remove the coating composition from the unexposed area; said photosensitive material being selected from the group consisting of light-sensitive dichromate and light-sensitive diazo compounds; said resinous copolymer containing in its formula both (*a*) polymerized olefinic hydrocarbon groups, and (*b*) at least one polymerized monomer group having a formula of the group consisting of:



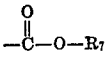
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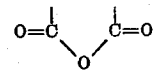
where R_4 is selected from the group consisting of a hydrogen atom and a methyl group and where R_5 and R_6 are independently selected from the group consisting of carboxyl groups of the formula:



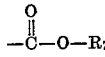
ester groups of the formula:



where R_7 is selected from the group consisting of alkyl groups, alkoxyalkyl groups, alkenyl groups, alkinyl groups, cycloalkyl groups and aryl groups, and an anhydride group of the formula:



formed by R_5 and R_6 collectively, with the further provision that 5–90% of the R_5 and R_6 groups are ester groups of the formula:



22. The method of forming a relief image which comprises: (1) preparing a coated surface by coating a surface with a photographic composition consisting essentially of a photosensitive material incorporated in a water-insoluble resinous copolymer, (2) exposing the coated surface to light with a replica of the relief image interposed between the light source and the coated surface, and (3) treating the coated surface with a solution to remove the coating composition from the unexposed area; said photosensitive material being selected from the group consisting of light-sensitive dichromate and light-sensitive diazo compounds; said resinous copolymer being a copolymer of (*a*) styrene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.6 molar proportion, per molar proportion of maleic anhydride, of an alkanol containing 1–8 carbon atoms in its structure.

23. The method for forming a relief image which comprises: (1) preparing a coated surface by coating a surface with a photographic composition consisting essentially of a light-sensitive dichromate compound incorporated in a water-insoluble resinous copolymer, (2) exposing the coated surface to light with a replica of the relief image interposed between the light surface and the coated surface, and (3) treating the surface with a solvent solution to remove the coating composition from the unexposed area; said resinous copolymer being a copolymer of (*a*) styrene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.6 molar proportion, per molar proportion of maleic anhydride, of an alkanol containing 1–8 carbon atoms in its structure.

24. The method of forming a relief image which comprises: (1) preparing a coated surface by coating a surface with a photographic composition consisting essentially of a light-sensitive diazo compound incorporated in a water-insoluble resinous copolymer; (2) exposing the coated surface to light with a replica of the relief image interposed between the light surface and the coated surface; (3) performing at least one of the following steps (*a*) and (*b*), (*a*) immersing the coated surface in an alkaline coupler solution and (*b*) exposing the coated surface to radiant heat; (4) immersing the coated surface in an alkaline solution; and (5) removing the coating from the area unexposed to light; said resinous copolymer being a copolymer of (*a*) styrene and (*b*) maleic anhydride; said copolymer being esterified with 0.1–0.15 molar

proportion, per molar proportion of maleic anhydride, of methanol and 0.35–0.45 molar proportion, per molar proportion of maleic anhydride, of butanol.

References Cited in the file of this patent

UNITED STATES PATENTS

1,981,102 Hagedorn et al. ---------- Nov. 20, 1934
2,616,851 Giammaria ---------- Nov. 4, 1952
2,719,141 Smith ---------- Sept. 27, 1955
2,835,656 Unruh et al. ---------- May 20, 1958

FOREIGN PATENTS

585,760 Great Britain ---------- Feb. 24, 1947