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54 Production of image-wise modified elements and material suitable therefor comprising a colloid layer containing polymers with oxime groups.

57 A radiation-sensitive material is described that comprises a hydrophilic colloid layer containing a dispersed phase of at least one radiation sensitive polymer the polymer chain of which comprises units with side substituents containing oxime ester groups. Upon imagewise exposure to actinic radiation of the polymer in the exposed areas reduces the permeability of the hydrophilic colloid layer for an etchant in the absence of any ethylenically unsaturated monomer. The layer having upon imagewise exposure to radiation image-wise differentiations in permeability for an etchant can be used as etch-resist, without needing a washing away step, to modify image-wise the surface of an element e.g. to produce printed circuits or printing forms.

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Production of image-wise modified elements and material
suitable therefor.

The present invention relates to a method and materials for producing image-wise modified elements. This
5 method and materials can be used e.g. in the production of printed circuits, in photochemical tooling, in the production of printing forms etc. According to this method the surface of an element or the element itself is modified image-wise. The image-wise modification of
10 an element or of its surface in conformity with an image-wise exposure occurs by means of an etchant, whose action is image-wise controlled by means of an etch-resist.

Various kinds of etch resists are known. In the preparation of printing forms especially the preparation
15 of gravure printing forms, the etch resist controls image-wise the action of the etchant so that the surface of the underlying printing member is modified image-wise so as to obtain more or less depressed areas.

The depressed areas or cavities will receive the
20 printing ink, which ink is transferred from these cavities or ink cells to the printing stock. The transfer of ink to the printing stock is e.g. due to the suction of the printing stock, the adhesion power and/or viscosity of the ink etc.

The etch resist controlling the action of the et-

chant on the underlying printing member may consist e.g. of a hardened relief pattern. The thinner said pattern, the more intense the etching, in other words the deeper the etchant attacks the element to be etched.

5 The overwhelming part of gravure printing is performed with the aid of carbon tissue or pigment paper. Carbon tissue or pigment paper comprises a gelatin layer, which is made sensitive to ultra-violet light by means of an aqueous solution of alkali- or ammonium dichromate.
10 After careful drying, the so-called "dichromated gelatin" layer is exposed e.g. through a continuous tone image and a gravure screen. The gelatin hardens in conformity with this exposure. The carbon tissue is then adhered to the printing surface, while pressure and moisture are
15 applied. By the action of water the gelatin layer swells and firmly adheres to the printing surface, which had been hydrophilized beforehand. Subsequently, the unexposed and thus unhardened gelatin is washed away with warm water, whereas the printing element remains covered
20 with an exposed and hardened etch resist forming a gelatin relief pattern. At this stage an etchant can be applied. The action of such etchant on the underlying printing element is proportional to the thickness of said relief pattern.

25 The quality of the printing form made by means of carbon tissue highly depends upon the skill of the working personnel and on the working conditions such as the temperature and the relative humidity. Moreover, pigment paper has two very important drawbacks, first the "dark
30 reaction", which initiates the hardening of the gelatin without any exposure and secondly the continued hardening of the exposed "dichromatic gelatin", even when the exposure has ceased. In spite of these drawbacks, gravure printing based upon carbon tissue provides good printing

quality, viz. high density printing values, good tone rendering, high runs, and consistent colour reproduction.

Because of the dependency on many variables it is necessary to simplify the preparation of gravure printing forms. It has been proposed therefore to use more consistent products and methods. For example in the US-Patent Specification 2,760,863 of Louis Plambeck Jr. issued August 28, 1956, a material is described, which comprises a layer consisting of a homogeneous mixture of a photopolymerisable ethylenically unsaturated monomer, a photoinitiator, and a binder. Upon image-wise exposure the monomers in the homogeneous mixture polymerize image-wise, whereas the unexposed areas remain unpolymerized. The unexposed areas are washed away.

Homogeneous mixtures of photopolymerizable monomers and of a photoinitiator in a binder are extremely sensitive to polymerization inhibiting phenomena caused by oxygen.

To overcome oxygen inhibition as occurs in the photopolymerization of photopolymerizable monomers homogeneously mixed with a photoinitiator in a hydrophilic colloid binder it has been proposed in the US Patent Specification 3,418,118 of Glen Anthony Thommes and Peter Walker issued December 24, 1968, to use a heterogeneous dispersion of photopolymerizable monomer and of photoinitiator in a hydrophilic colloid binder.

In the US Patent Specification 3,718,473 of Joseph Edmund Gervay and Peter Walker issued February 27, 1973 a material for forming an etch resist is described which comprises a hydrophilic colloid layer including a dispersed phase of an ethylenically unsaturated monomer and a free-radical photoinitiator. Upon image-wise exposure, image-wise photopolymerization takes place so that the diffusibility of an etchant through the binder layer is

reduced image-wise. The image-wise polymerization of this material changes the chemical and physical behaviour of the heterogeneous layer. In the process according to the above-mentioned Patent Specification there is no need to
5 wash away the unpolymerized monomers.

In the above procedures of making etch resists based on the photoinitiated polymerization of ethylenically unsaturated monomers all kinds of photoinitiators can be used.

10 Non-polymeric as well as polymeric compounds containing oxime ester groups are known from US Patent Specification 3,558,309 of Urbain Leopold Laridon and Gérard Albert Delzenne issued January 26, 1971 for use as photoinitiator in the photopolymerization of ethylenically un-
15 saturated monomers and to make etch resists with the washing-away step according to the method of the above US Patent 2,760,863. These photoinitiators can of course also be used in the procedure of the above US Patent Specification 3,718,473 without washing away step.

20 According to UK Patent 1,180,845 filed August 8, 1967 by Gevaert-Agfa N.V., etch resist can be made by image-wise photodegradation of polymers containing oxime ester groups and washing away the decomposed polymer in the exposed areas by means of solvents in which the non-
25 decomposed polymer in the unexposed areas is insoluble.

Surprisingly, it has been found that a hydrophilic colloid layer containing a dispersed phase of a polymer with recurring units containing oxime ester groups in the side-chain can be used to form an etch resist, through
30 which after image-wise exposure an etchant diffuses image-wise, without the need of a washing away step before the application of the etchant and without the presence of an ethylenically unsaturated monomer in the layer.

The present invention thus provides a process for

image-wise modifying the surface of an element by making an etchant diffuse through a layer applied to said surface, this layer forming an etch resist with image-wise differentiations in permeability for an etchant. The
 5 said etch resist is formed by the steps of image-wise exposing to actinic radiation a layer of a hydrophilic colloid binder containing, in the absence of any ethylenically unsaturated monomeric material, a dispersed phase of at least one radiation-sensitive polymer, the
 10 polymer chain of which comprises units with side-substituents containing oxime ester groups. By the exposure to actinic radiation the permeability of the layer for an etchant is reduced in conformity with said exposure.

The phenomenons taking place in the process of the
 15 present invention are believed to be the following. The hydrophilic binder medium wherein a polymer, whose polymer chain comprises units with side-substituents containing oxime ester groups, is heterogeneously dispersed, constitutes the medium, through which an etchant e.g.
 20 an Fe(III)chloride solution can diffuse in consequence of the capillary behaviour of said medium. Upon exposure to actinic radiation the oxime ester units in said polymer form radicals which crosslink with the hydrophilic binder medium so that the capillarity of the layer is
 25 reduced and thus the permeability of the layer for a hydrophilic etchant is reduced.

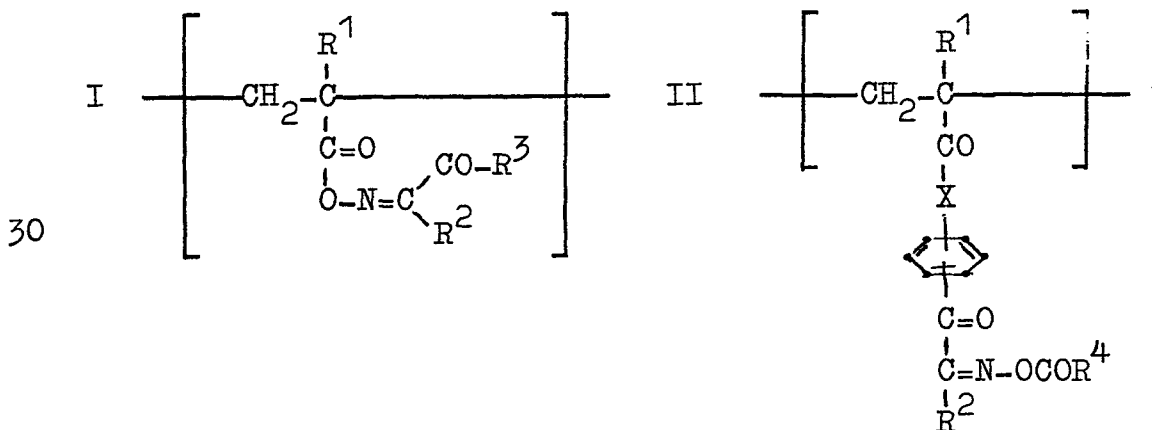
By the term oxime ester group is meant an O-acyl-oxime group of the formula $\text{>C} = \text{N} - \text{O} - \text{CO} - \text{R}$ wherein R is an organic group.

30 Particularly suitable polymeric compounds having side-substituents comprising an oxime ester group are polymers obtained by (1) the reaction of a monooxime of an α, β -diketone e.g. 1-phenyl-1,2-propanedione-2-oxime, 1-(p-hydroxyphenyl)-1,2-propanedione-2-oxime,

p-hydroxyphenyl glyoxalaldoxime and 2,3-butanedione mono-oxime with an ethylenically unsaturated acid chloride e.g. acryloyl or methacryloyl chloride and polymerization or copolymerization of the thus formed monomer carrying an oxime ester group, or (2) the reaction of an ethylenically unsaturated compound comprising an α, β -diketo monooxime, with a carboxylic acid chloride which includes an aliphatic, aromatic or heterocyclic acid chloride e.g. acetylchloride, propionylchloride, benzoylchloride, p-nitrobenzoyl chloride, o-methoxybenzoyl chloride, o-chlorobenzoyl chloride, 2-methyl-3-indolizine carbonyl chloride, etc., and polymerization or copolymerization of the thus formed monomer carrying an oxime ester group. These polymers are thus polymers or copolymers of monomers corresponding to the formula $M^1COON=C-COM^2$ wherein one of M^1 and M^2 is or comprises an R ethylenically unsaturated group and the other is an aliphatic, aromatic or heterocyclic group e.g. alkyl including substituted alkyl or aryl including substituted aryl and R represents hydrogen, alkyl including substituted alkyl or aryl including substituted aryl.

Particularly suitable polymers are those comprising recurring units corresponding to one of the following general formulae I and II :

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wherein :

R^1 is hydrogen or C_1-C_5 alkyl e.g. methyl,

R^2 represents hydrogen, alkyl including substituted alkyl or aryl including substituted aryl,

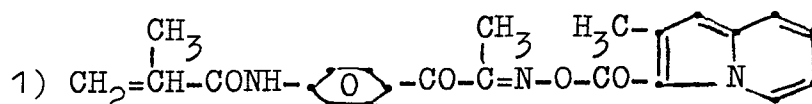
5 R^3 represents alkyl including substituted alkyl, aryl including substituted aryl,

X represents -NH- or -O-, and

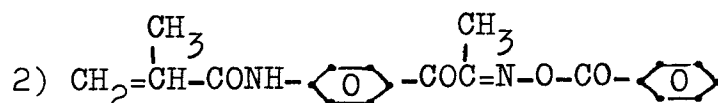
R^4 represents an aliphatic, aromatic, or heterocyclic group.

The polymers used according to the present invention
10 can be homopolymers or copolymers. They are preferably copolymers comprising besides the units with oxime ester group in the side chain units derived from a variety of monomers, whereof preferably at least one is hydrophobic. Examples of comonomers are (meth)acrylamide, N-alkyl(meth)
15 acrylamide, alkyl(meth)acrylate, styrene, acrylonitrile, N-vinylpyrrolidone, vinyl acetate and other vinyl esters. Preferred copolymers comprise from 5 to 50 mol % recurring units with oxime ester groups in the side chain.

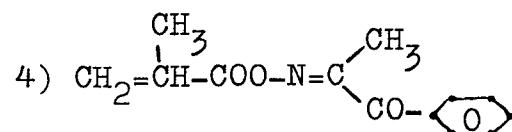
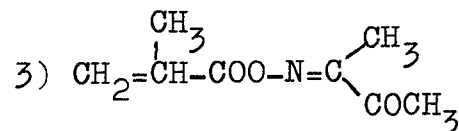
Representative examples of monomers from which the
20 polymers used according to the invention can be derived are :

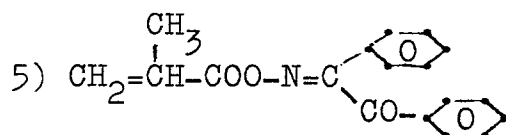


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Preparation of the latter three monomers and polymerization thereof is illustrated in UK Patent 1,180,845, already mentioned hereinbefore.

The following preparations illustrate how monomers 1) and 2) are prepared.

Preparation 1 : Monomer 1).

10 a) p-propionyl-acetanilide :

1290 g of aluminium chloride (9.6 mole) were suspended with stirring in 1500 ml of carbon disulphide. 405 g of acetanilide (3 moles) were added slowly to this suspension, while the temperature was kept at 25°C. The reaction mixture was heated until reflux and was cooled immediately to 25°C. 565 ml of propionyl chloride (6.5 moles) were added dropwise in such a way that the temperature was kept at 25°C. The reaction mixture was heated until reflux for 5 hours and kept overnight at ambient temperature (20°C).

20 The supernatant carbon disulphide layer was decanted and the remaining viscous mixture was poured in a mixture of ice and hydrochloric acid. The residue formed was filtered off and further recrystallized from a mixture of 1500 ml of ethanol and 75 ml of water. Drying was applied under vacuum at 100°C. A light yellow powder was obtained.

Yield : 400 g.

Melting point : 165°C.

b) p-propionyl aniline :

141 g (1 mole) of p-propionylacetanilide were dissolved while refluxing and stirring into 600 ml of 5N hydrochloric acid. Refluxing was continued for 30 min, cooling was applied, and sodium carbonate (about 300 g) was added, until the reaction mixture was alkaline. The

residue formed was sucked off, washed with water until neutral and recrystallized from 725 ml of isopropanol. The mixture was sucked off and washed with ether. After drying under vacuum, a yellow-brownish powder was obtained. Yield : 126 g (85 %).

Melting point : 138°C.

c) N-p-propionylphenyl-methacrylamide :

149 g (1 mole) of p-propionylaniline were dissolved in 1250 ml of dioxan with stirring and heating.

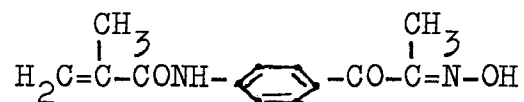
10 The solution was cooled to 25°C and 92.4 g of sodium hydrogen carbonate (1.1 mole) were added.

A small amount of m-dinitrobenzene and copper(II) acetate were added whereupon a solution of 124.5 g of methacrylyl chloride (1 mole) in 125 ml of dioxan were added dropwise. The temperature was kept at 20-25°C. Stirring was then continued for 30 min whilst slowly heating until reflux. Light yellow needles were sucked off, washed with ether, and dried under vacuum. Yield : 130 g.

20 Melting point : 132°C.

The filtrate was evaporated to $\frac{1}{4}$ of its volume and the residue was sucked off, washed with ether, and dried under vacuum. Another 67 g of light-yellow needles melting at 132°C were obtained.

25 d) compound of the formula :



217 g (1 mole) of N-p-propionylphenyl-methacrylamide were dissolved in 1500 ml of trichloromethane with stirring and slight heating.

The mixture was cooled to ambient temperature (20°C). Dry hydrogen chloride was introduced for 15 min and simultaneously a solution of 200 ml of n-amyl nitrite in 200 ml

of trichloromethane were added dropwise. The temperature was kept between 20 and 26°C. Subsequently, hydrogen chloride was introduced for another 15 min with stirring. The resulting mixture was allowed to stand overnight.

- 5 The residue formed was sucked off and dried under vacuum. A light-yellow powder was obtained.

Yield : 205 g (83 %).

Melting point : 210°C.

- This product may be purified by dissolving in a 10% aqueous solution of sodium hydroxide and again forming a residue with HCl or by recrystallization from a mixture of ethanol and water (2:1)

e) 2-methylindolizine :

- A mixture of 92.5 g monochloroacetone (1 mole) and 15 93 g of α -picoline (1 mole) was heated for 2½ h on a boiling water-bath. The reaction mixture was cooled to ambient temperature (20°C) and kept overnight. A solid black mass formed. Extraction was performed on a hot water-bath until the mass had dissolved completely (about 20 700 ml). The solution was filtered and washed 3 times with 100 ml of ether. A few ml of an aqueous saturated sodium carbonate solution were added and the solution was then washed again 4 times in ether. 150 g of solid sodium hydrogen carbonate was added carefully and steam 25 distillation was carried out. The distillate was cooled and sucked off. The solid product was dissolved quickly in ether and dried on heated magnesium sulphate. The ether was evaporated and the residue dried.

Yield : 165 g (65 %).

- 30 Melting point : 65°C.

After steam distillation the product was to be shielded from light.

f) 2-methyl-indolizine-3-carbonyl chloride :

A solution of 99 g of phosgene (1 mole) in 800 ml

of anhydrous toluene was cooled beneath 15°C. While the reaction mixture was cooled and stirred a solution of 131 g of methyldolizine (1 mole) in 475 ml of anhydrous toluene was added dropwise. The reaction mixture was kept 5 overnight and the residue formed was sucked off.

The filtrate was evaporated to dryness and the residue was recrystallized from 1 litre of anhydrous hexane. The mixture was sucked off and dried under vacuum. Yellowish-green needles were obtained.

10 Yield : 97 g (50 %).

Melting point : 71°C.

The product was stable for some weeks at 0°C.

g) monomer 1 :

4.92 g (0.02 mole) of the compound of step d) were 15 dissolved with stirring in 25 ml of 1N sodium hydroxide.

A small amount of triphenylmethyldarsoniumiodide was added and the mixture was cooled in ice-water until the temperature was between 0°C and 5°C. A solution of 3.87 g (0.02 mole) of 2-methyl-indolizine-3-carbonyl chloride 20 (step f) in 50 ml of methylene chloride was added dropwise in 5 min.

Stirring was continued for 30 min at 0-5°C and subsequently at ambient temperature for 2 h. During this operation the pH was checked continuously. The reaction 25 mixture should remain strongly alkaline.

A supplemental amount of 50 ml of methylene chloride was added and the water layer was decanted.

The mixture was washed a few times with water and the methylene chloride layer was evaporated under vacuum.

30 The residue was washed with a small amount of ether, sucked off, and dried under vacuum. A yellowish green powder was obtained.

Yield : 6.1 g (75 %). Melting point : 157°C.

The product should be shielded from light during and

after the reaction. If necessary the product can be purified by recrystallization from a mixture of ethanol and water (90:10 by volume). Elementary analysis :

	Calc. C 68.59	found C 66.35-65.95
5	H 5.21	H 5.10-5.00
	N 10.42	N 10.00-10.05

Preparation 2 : monomer 2

Monomer 2 was prepared as monomer 1 (step g of preparation 1 using 2.81 g of benzoyl chloride).

10 The above monomers can be homopolymerized or copolymerized to form polymers with recurring units containing an oxime ester group in the side chain as is illustrated in Research Disclosure June 1973, Havant, England, Disclosure No. 11048 and by the following preparations.

15 Preparation 3 : Copolymer of methylmethacrylate and monomer 2

3 g of azobis-isobutyronitrile were added to a solution of 70 g of monomer 2 and 80 g of methyl methacrylate (0.8 mole) in 750 ml of dimethylformamide. The solution
20 was stirred under nitrogen atmosphere at 75°C for 24 hours. The viscous solution was allowed to form a residue in methanol and the polymer obtained was separated and sucked off under vacuum.

During and after the reaction the product was shielded
25 from light.

Yield : 135 g (90 %) $[\eta]_{\text{THF}} = 0.15-0.20$

The molar ratio of methylmethacrylate units to monomer units 2 was 81:19.

30 Preparation 4 : Copolymer of methylmethacrylate and monomer 1

3 g of azobis-isobutyronitrile were added to a solution of 40.45 g of monomer 1 (0.15 mole) and 85 g of methyl methacrylate (0.85 mole) in 750 ml of dimethylformamide.

The solution was stirred in nitrogen atmosphere at 75°C

for 24 h. The viscous solution was allowed to form a residue in methanol and the polymer obtained was sucked off and dried under vacuum. The product was shielded from light during and after the reaction.

5 Yield : 123 g. $[\eta]_{\text{THF}} = 0.10$

The molar ratio of methylmethacrylate units to monomer units 1 was 85:15.

The resist-forming layer used according to the present invention comprises dispersed in a hydrophilic col-
10 loid binder in the absence of any ethylenically unsaturated monomeric material, at least one radiation sensitive polymer comprising units with oxime-ester groups as side substituents.

The hydrophilic colloid used as the binder for the
15 dispersed polymer particles is preferably gelatin, but other hydrophilic colloids can also be used, e.g. colloidal albumin, alginic acid and derivatives thereof, a cellulose derivative e.g. carboxymethylcellulose and hydroxyethylcellulose, a synthetic hydrophilic colloid such as
20 polyvinyl alcohol, poly-N-vinyl pyrrolidone, copolymers of acrylic acid, polyacrylamides and derivatives, etc. If desired, compatible mixtures of two or more of these colloids can be employed for dispersing the polymer particles.

25 The weight ratio of hydrophilic colloid to polymer is preferably comprised between 20:1 and 1:1.

The radiation-sensitive polymers can be dispersed in the hydrophilic colloids using any of the dispersion techniques known for incorporating photographic ingredients
30 e.g. colour couplers in silver halide emulsion layers. A particularly suitable technique is to disperse the polymers from solutions in high-boiling water-immiscible solvents or mixtures of high-boiling and low-boiling water-immiscible solvents, in aqueous solutions of the hydro-

philic colloid. Examples of such high-boiling solvents are tricresyl phosphate, dibutyl phthalate and other esters of organic dicarboxylic acids e.g. diethylmalonate, diethyloxalate, diethyl succinate, etc. In dispersing
5 the polymer droplets in the aqueous colloid surfactants can be used which include anionic, non-ionic and amphoteric compounds, e.g. sodium alkyl naphthalene sulphonates, sodium lauryl sulphate, sulphonated derivatives of fatty acid amides, sodium dioctylsulphate, sodium isotetradecyl
10 sulphate, sorbiton monolaurate, etc.

By the use of the high-boiling water-immiscible solvents the polymers are dispersed in the hydrophilic colloid medium in the form of oily droplets. The average diameter of these droplets may be comprised between 0.01
15 and 20 microns preferably between 0.05 and 5 microns.

It is also possible to disperse the polymers in the aqueous colloid compositions from solutions in low-boiling water-immiscible solvents and removing the solvent during or after dispersing by evaporation if necessary under re-
20 duced pressure.

The radiation sensitive resist-forming layer used according to the present invention may comprise in addition to the binder and radiation sensitive polymer, compounds increasing the sensitivity e.g. Michler's ketone
25 and analogous aromatic ketones which increase the spectral response especially in the range of 270 to 380 μm .

The layer may also comprise so-called "filler"-compounds that are substantially non light-sensitive and do not crosslink with the hydrophilic binder. Such filler
30 compounds are e.g. co(ethylene glycol isophthalate/isopropylene glycol isophthalate 50:50), co(vinyl chloride/vinyl acetate/maleic acid anhydride), co(vinyl acetate/vinyl chloride), co(vinyl chloride/vinyl acetate/maleic acid), polyvinyl-n-butyral, polyisobutyl methacrylate,

polystyrene, polymethyl methacrylate, cellulose acetate butyrate, co(styrene/butadiene), and an epoxy resin of bisphenol A and epichlorohydrin, marketed by Ciba-Geigy, Basel, Switzerland under the name of ARALDITE GY 250
5 being preferred.

The layer may also contain antioxidizing agents, coating aids, dyes, etc.

In order to visualize the differentiation in diffusibility for an etchant of the radiation-sensitive layer
10 after exposure it is possible to incorporate in the layer all sorts of radiation-sensitive compounds which change colour or produce a colour upon exposure. For this purpose it is preferred to use polymers with ketoxime groups as side-substituents in recurring units that upon
15 exposure to actinic radiation form coloured degradation products. An example of such polymer is the polymer of preparation 4 hereinbefore.

Visualization of the exposure phenomena makes possible sensitometric evaluation and follow up of the subsequent etching. Moreover by colouring during exposure, sensitivity decreases by the filtering action and the gradation decreases which is favourable for continuous-tone reproduction.

The resist-forming radiation-sensitive layer can be
25 applied to any substrate known in the art. Metal supports or supports coated with metals such as for example zinc, and especially aluminium are excellently suited as base materials for a planographic printing plate. For the production of a planographic printing plate there may be
30 likewise used specially treated sheets of paper or polymeric film supports coated with a metallic layer. For use in the production of intaglio or relief printing plates metal base materials suited for etching are used e.g. metal plates or cylinders of zinc, copper, steel or an

etchable magnesium alloy. For use in the production of printed circuits the photoresist composition is applied e.g. to a supported copper layer, which can be easily etched.

5 The present radiation-sensitive layers can likewise be used in the production of microimages. For that purpose the photoresist coatings are applied to a relatively thin highly opaque black or grey metal coating that can be etched and serves as imaging layer. Suited metal
10 coatings are made of tellurium or a tellurium alloy having a thickness in the range of 50 nm to 500 nm or bismuth coatings having a thickness in the range of 25 nm to 300 nm.

 According to one embodiment in the composition of
15 the metallic imaging layer tellurium alloys comprising at least 50 atomic percent of tellurium are used. Typical tellurium compositions, which are etchable with an opaque hypochlorite solution are described in US Patent Specifications 3,271,591 and 3,530,441 of Stanford R.Ovshinsky
20 issued respectively September 6, 1966 and September 22, 1970.

 According to another embodiment the imaging metal layer consists of bismuth. Bismuth possesses the advantage of directly adhering to organic resin supports such
25 as a polyethylene terephthalate support when deposited thereon from bismuth vapour under reduced pressure conditions.

 Vapour deposition techniques are sufficiently known to those skilled in the art e.g. of preparing photocon-
30 ductive selenium coatings (see e.g. US Patent Specifications 3,874,917 of Charles Wood, John C.Schottmiller and Francis W.Ryan issued April 1, 1975 and 3,884,688 of John C.Schottmiller, Francis W.Ryan and Charles Wood issued May 20, 1975).

For the etching of the bismuth layer preference is given to aqueous acidic iron(II) chloride solution. The concentration of iron(III) chloride is e.g. in the range of 5 to 20 % by weight. Said solution contains preferably from 0.25 to 1 % by weight of citric acid.

A likewise useful etching solution for the removal of bismuth is an aqueous solution containing 3 to 6 % by weight of hydrogen peroxide and 5 to 10 % by weight of sulphuric acid.

10 The radiation-sensitive layers according to the invention can be applied to the surfaces to be modified by any known coating technique e.g. by spin-coating, whirl coating, spraying, dip-coating, roller coating, air-knife coating, doctor-blade coating etc.

15 Instead of applying the radiation-sensitive layer directly to the surfaces to be modified they can be provided on a temporary support from which they can be stripped off if necessary by means of a stripping layer before or after exposure, and transferred to the surface to be
20 etched. Preferred temporary supports are transparent film supports which permit exposure through the support. Examples of such transparent supports are cellulose nitrate film, cellulose ester film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film and
25 related films of resinous materials. Other suitable temporary supports are paper and paper, which has been coated with α -olefin polymers, e.g. polyethylene, polypropylene, polyisobutylene-polyethylene mixtures etc.

It is possible to provide an antihalation layer between the radiation-sensitive layer and the temporary
30 support e.g. between the stripping layer and the support or between the radiation sensitive layer and the stripping layer. It is also possible to provide the antihalation layer on the side of the transparent support opposite to

that carrying the radiation-sensitive layer.

The exposure of the radiation-sensitive resist forming layer preferably occurs by means of UV-radiation sources e.g. carbon arcs and mercury vapour lamps. Exposure may
5 occur through a contacted transparent master pattern or by a projection exposure.

The following examples illustrate the present invention.

Example 1

An aqueous phase containing 60 g of gelatine, 340 g of
10 water, 40 g of a 5 % aqueous solution of the sodium salt of diisooctyl sulphosuccinate was prepared as follows : gelatin was allowed to swell for 1 h in water and then heated to 50°C, whereupon the other ingredients of the aqueous phase were added.

15 Next, an oily phase was prepared by dissolving 30 g of tricresyl phosphate, 3 g of Michler's ketone and 20 g of co(ethylene glycol isophthalate/isopropylene glycol isophthalate) (50:50) in 90 g of ethyl acetate and 90 g of m-xylene and then dissolving therein 40 g of the poly-
20 mer of preparation 4.

The oily phase was emulsified in the aqueous phase by means of an homogenizer. Then 760 ml of water and 12.5 g of aqueous formaldehyde (4 % by weight) were added to obtain the desired viscosity.

25 The emulsion was dip-coated on a polyethylene terephthalate support and dried. The thickness of the coated layer varied from 5 to 10 μm .

Preparation of the coating composition and coating occurred under darkroom illumination. The image-wise
30 exposure was performed in contact in a vacuum frame in two stages. An exposure was carried out through a gravure screen of 65 lines per cm, in which the ratio of the dark lines to the transparent parts was 1:2.5.

Another exposure occurred through a continuous

tone positive. The light source used was a mercury vapour lamp. The time relation between the continuous tone exposure and the screen exposure was 0.66:1.

After the exposure, the etch resist layer showing a brown negative image was transferred by pressure to a wet copper surface. The polyethylene terephthalate support was stripped off and the etch resist was dried in the air.

The parts of the copper surface that were not covered by etch resist were coated with an asphalt derivative. The etching was performed with an iron(III)chloride solution of 39-43° Baumé for about 15 min.

The etching was stopped by abundantly rinsing with hot water. The etch resist was rubbed off easily. The resulting etch depths reached 3 to 45 μm . No undercutting was observed.

Example 2

Example 1 was repeated with the difference that the aqueous phase contained :

	gelatin	90 g
20	water	550 g
	5 % aqueous solution of the sodium salt of diisooctyl sulphosuccinate	60 g

and the oil phase contained :

	ethyl acetate	135 g
25	m-xylene	135 g
	tricresyl phosphate	45 g
	Michler's ketone	4.5 g
	co(ethylene glycol isophthalate/isopropylene glycol isophthalate (50:50)	30 g
30	polymer of preparation 3	30 g
	polymer of preparation 4	3 g

The oily phase was dispersed in the aqueous phase and after dilution as in example 1 coated on a polyethylene

terephthalate support.

Exposure, transfer and etching occurred as described in Example 1.

- 1 -

WHAT WE CLAIM IS :

1. Process for image-wise modifying the surface of an element e.g. to produce a printing form by making an etchant diffuse through a layer applied to said surface, 5 the said layer forming an etch resist with image-wise differentiations in permeability for etchants characterized in that said etch resist is formed by the steps of image-wise exposing to actinic radiation a layer of a hydrophilic colloid binder containing in the absence 10 of any ethylenically unsaturated photopolymerisable monomeric material, a dispersed phase of at least one radiation sensitive polymer the polymer chain of which comprises units with side substituents containing oxime ester groups, whereby the permeability of the hydrophilic 15 colloid layer for an etchant is reduced in conformity with the image-wise exposure.

2. Process according to claim 1, wherein the said radiation-sensitive polymer is a homopolymer or copolymer derived from a monomer corresponding to the formula :

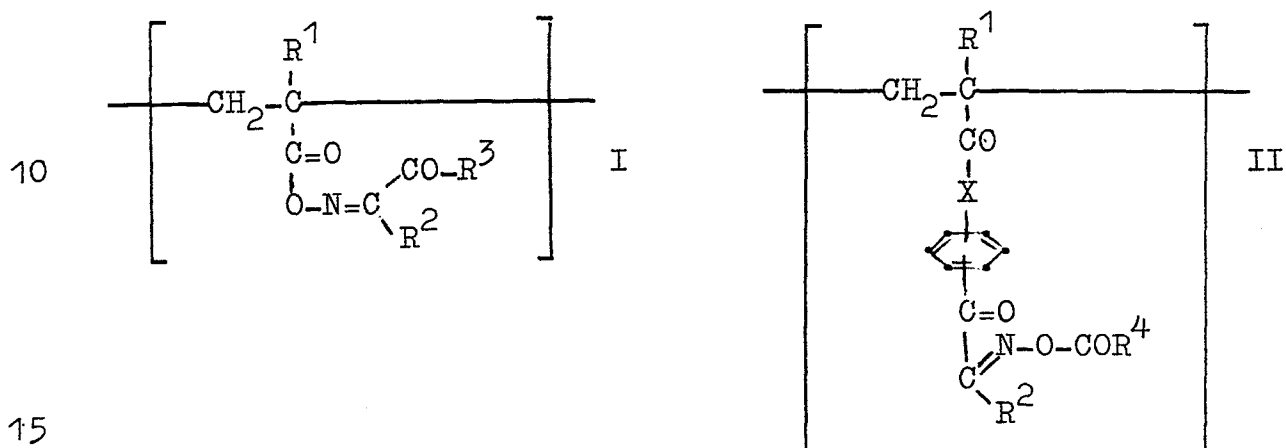


wherein :

one of M^1 and M^2 is or comprises an ethylenically unsaturated group, and the other is an aliphatic, aromatic 25 or heterocyclic group, and

R represents hydrogen, alkyl including substituted alkyl, or aryl including substituted aryl.

3. Process according to claim 2, wherein the radiation-sensitive polymer comprises recurring units corresponding to one of the following formulæ I and II :



wherein :

R^1 is hydrogen or C_1 - C_5 -alkyl,

R^2 represents hydrogen, alkyl including substituted alkyl or aryl including substituted aryl, and

R^3 represents alkyl including substituted alkyl or aryl including substituted aryl,

X represents -NH- or -O-,

R^4 is an aliphatic, aromatic or heterocyclic group.

4. Process according to any of claims 1 to 3, wherein the polymer is a copolymer comprising from 5 to 50 mole % recurring units with oxime ester groups in the side chain.

5. Process according to any of claims 1 to 4, wherein the polymer is a copolymer comprising recurring alkyl-(meth)acrylate units.

6. Process according to any of the preceding claims, wherein the ratio of hydrophilic colloid to radiation-sensitive polymer is comprised between 20:1 and 1:1.

7. Process according to any of the preceding claims, wherein the etch-resist forming layer is applied to the surface to be modified after exposure of the said layer carried by a temporary support which is stripped off after
5 transfer of the layer to the said surface to be modified.

8. A radiation sensitive material comprising a support and a hydrophilic colloid layer characterised in that the hydrophilic colloid layer contains, in the absence of any ethylenically unsaturated photopolymerisable
10 monomeric material, a dispersed phase of at least one radiation sensitive polymer the polymer chain of which comprises units with side substituents containing oxime ester groups, the said polymer being capable by exposure to actinic radiation of reducing the permeability of the
15 hydrophilic colloid layer for an etchant.

9. Material according to claim 8, wherein the said radiation-sensitive polymer is a homopolymer or copolymer derived from a monomer corresponding to the formula :



wherein :

one of M^1 and M^2 is or comprises an ethylenically unsaturated group, and the other is an aliphatic, aromatic or heterocyclic group, and
25 R represents hydrogen, alkyl including substituted alkyl, or aryl including substituted aryl.

10. Material according to claim 8 or 9, wherein the polymer is a copolymer comprising from 5 to 50 mole % recurring units with oxime ester groups in the side
30 chain.

11. Material according to claim 8, 9 or 10, wherein the polymer is a copolymer comprising recurring alkyl-(meth)acrylate units.

12. Material according to any of the preceding claims 8 to 11, wherein the ratio of hydrophilic colloid to radiation-sensitive polymer is comprised between 20:1 and 1:1.



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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>US - A - 3 558 309</u> (U.L.LARIDON et al.) * Column 1, line 45 to column 4, line 29; column 4, line 66 to column 5, line 12 *		G 03 C 1/68 G 03 F 7/10
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A	<u>US - A - 3 558 311</u> (G.A.DELZENNE et al.) * Column 1, line 18 to column 3, line 58; the claims 1-6 *		
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A	<u>FR - A - 2 011 046</u> (GEVAERT-AGFA)		TECHNICAL FIELDS SEARCHED (Int.Cl. ²)
A	<u>US - A - 3 484 238</u> (R.D.FOX)		
A	<u>US - A - 3 255 002</u> (H.G.ROGERS)		G 03 C 1/68 G 03 F 7/10
A	<u>US - A - 3 306 744</u> (H.C.HAAS)		

			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
X The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 18-08-1978	Examiner RASSCHAERT