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The invention relates to a process for the production of relief copies, in which the light-sensitive layer of a light-hardenable copying material, which layer contains a photopolymerizable mixture, a photodimerizable
5 polymeric compound or a negative-working light-sensitive diazo compound, is exposed imagewise, and the unexposed areas of the layer are washed out by means of a developer.

Such light-hardenable materials, in particular the photopolymerizable materials, are, in most cases, not yet
10 fully hardened after the imagewise exposure. It has been found that depending on the interval between exposure and development, there are distinct differences in the wedge length of copied continuous-tone step wedges. These variations are particularly pronounced in the case of
15 exposure with laser light, for example from an argon ion laser.

The earlier German Patent Application P 30 45 149 (published 1st July, 1982) already proposes a process by means of which these disadvantages can be avoided. The process
20 comprises warming the initially mentioned light-sensitive material, during the exposure or after the exposure, for a short time at an elevated temperature and then developing.

It was the object of the invention to propose a process of the initially mentioned generic type which makes
25 it possible, when processing the initially mentioned materials, always to arrive at constant results, and to manage with less exposure.

The invention is based on a process for the preparation of relief copies, in which the light-hardenable layer of a copying material, which layer contains a photopolymerizable mixture, a photodimerizable polymeric compound or a diazonium salt polycondensation product, is exposed imagewise and thereafter the unexposed areas of the layer are washed out by means of a developer.

The process according to the invention comprises subjecting the layer briefly to ultrasonic treatment after exposure, and then developing it.

The ultrasonic treatment is preferably effected as soon as possible after exposure, ie. within a period of up to about one hour after exposure.

The temperature in the ultrasonic bath should be between 4 and 50°C, preferably between 15 and 30°C.

The duration of the ultrasonic treatment can be between 5 seconds and 40 minutes, preferably between 30 seconds and 15 minutes.

The shorter the time interval between exposure and ultrasonic treatment, the shorter the duration of the ultrasonic treatment can be.

The ultrasonic treatment can be effected in a manner which is in itself known, for example by immersing the exposed plates in one of the commercially available ultrasonic baths, for example in an USIG-1500 (19-21 kHz, 1500 W) from Messrs. Schoeller Schall or in the type 12 (50 kHz, 60 W) from Messrs. Branson.

The light-sensitive materials to be processed by the method according to the invention are composed of a

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light-sensitive layer which is preferably present on a layer support.

Preferred light-sensitive layers are photopolymerizable layers. These contain, as essential constituents, a polymerizable compound having at least two terminal ethylenically unsaturated double bonds, a polymeric binder and a photoinitiator which, under the action of actinic radiation, is capable of initiating the free radical polymerization of the ethylenically unsaturated compound.

As further constituents, the layer can contain stabilizers or inhibitors to prevent the dark polymerization of the monomers, hydrogen donors, wetting agents, plasticizers, sensitometric regulators, dyestuffs and colorless or colored pigments.

A plurality of substances are suitable photoinitiators, for example benzoin, benzoin ether, polynuclear quinones, for example 2-ethyl-anthraquinone; acridine derivatives, for example 9-phenylacridine, 9-p-methoxyphenylacridine, 9-acetylaminoacridine and benz(a)acridine; phenazine derivatives, for example 9,10-dimethylbenzo(a)-phenazine, 9-methylbenzo(a)phenazine and 10-methoxybenzo(a)phenazine; quinoxaline derivatives, for example 6,4',4''-trimethoxy-2,3-diphenylquinoxaline and 4',4''-dimethoxy-2,3-diphenyl-5-aza-quinoxaline; quinazoline derivatives, synergistic mixtures of various ketones, dye-stuff/redox systems, thiopyrylium salts and the like.

The photoinitiators are in general used in an amount of 0.01 to 10, preferably of 0.2 to 5 % by weight, relative to the constituents of the photopolymerizable

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layer.

Photopolymerizable monomers suitable for the purposes of the invention are known and are described, for example, in U.S. Patents 2,760,863 and 3,060,023.

5 Preferred examples are acrylic acid esters and methacrylic acid esters, such as diglycerol diacrylate, polyethylene glycol dimethacrylate, and acrylates and methacrylates of trimethylolethane, trimethylolpropane, pentaerythritol and polyhydric alicyclic alcohols. Reaction
10 products of diisocyanates with partial esters of polyhydric alcohols can also be used with advantage. Such monomers are described in DE-A 20 64 079 and in DE-A 23 61 041.

The proportion of monomers in the layer is in
15 general about 10 to 80, preferably 20 to 60, % by weight.

The hydrogen donors used are, in the main, aliphatic polyethers. Where appropriate, this function can also be performed by the binder or by the polymerizable monomer, if these possess labile hydrogen atoms.

20 A plurality of soluble organic polymers can be employed as binders. As examples there may be mentioned polyamides, polyvinyl esters, polyvinyl acetals, polyvinyl ethers, epoxide resins, polyacrylic acid esters, polymethacrylic acid esters, polyesters, alkyd resins, polyacrylamide, polyvinyl alcohol, polyethylene oxide, polydimethyl-
25 acrylamide, polyvinylpyrrolidone, polyvinylmethylformamide, polyvinylmethacetamide and copolymers of the monomers which form the homopolymers mentioned.

Further suitable binders are natural materials or

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modified natural materials, for example gelatin, cellulose ethers and the like.

It is particularly advantageous to use binders which are insoluble in water but are soluble or at least swellable in aqueous alkaline solutions, since layers containing such binders can be developed with the preferred aqueous alkaline developers. Such binders can, for example, contain the following groups: $-\text{COOH}$, $-\text{PO}_3\text{H}_2$, $-\text{SO}_3\text{H}$, $-\text{SO}_2\text{NH}-$, $-\text{SO}_2-\text{NH}-\text{CO}-$ and the like. As examples of these binders there may be mentioned maleate resins, polymers of β -methacryloyloxyethyl N-(p-tolylsulfonyl)-carbamate, and copolymers of these and similar monomers with other monomers, as well as styrene/maleic anhydride copolymers. Methyl methacrylate/methacrylic acid copolymers and copolymers of methacrylic acid, alkylmethacrylates and methylmethacrylate and/or styrene, acrylonitrile and others, as described in DE-A 20 64 080 and in DE-A 23 63 806, are preferred.

The amount of binder is in general 20 to 90, preferably 40 to 80, % by weight of the constituents of the layer.

It is in general advantageous largely to shield the photopolymerizable layer from the influence of atmospheric oxygen during the photopolymerization, i.e., above all, prevent the continued diffusion of atmospheric oxygen into the layer. This is particularly important if the process is carried out without a vacuum copying frame, for example in the case of exposure by projection or by means of laser radiation. If the mixture is used in the form of

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thin copying layers it is advisable to apply a suitable covering film which is of low permeability to oxygen. This film can be self-supporting and can be peeled off before developing the copying layer. Polyester films, for example, are suitable for this purpose. The covering film can also be composed of a material which dissolves in the developer liquid or can, at least in the non-hardened areas, be removed during development. Suitable materials for this purpose are, for example, waxes, polyvinyl alcohol, polyphosphates, sugars and the like.

Suitable photodimerizable substances are, above all, cinnamic acid derivatives, especially cinnamic acid esters of polyhydroxy compounds, such as polyvinyl cinnamate. Copying materials of this type are described in GB-A 695,197.

Copying materials based on diazonium salt polycondensation products can also be used.

Suitable diazonium salt polycondensation products are condensation products of condensable aromatic diazonium salts, for example of diphenylamine-4-diazonium salts, with aldehydes, preferably with formaldehyde. It is particularly advantageous to use co-condensation products which in addition to the diazonium salt units also contain other units which are not sensitive to light and which are derived from condensable compounds; especially aromatic amines, phenols, phenol-ethers, aromatic thioethers, aromatic hydrocarbons, aromatic heterocyclics and organic acid amides. These condensation products are described in US-A 3,867,147. Generally, all diazonium salt

polycondensation products described in US-A 4,186,017 are suitable.

The light-sensitive layers of these copying materials can in addition contain binders, dyestuffs, indicators, pigments, stabilizers, wetting agents and other customary additives. The binders can be water-soluble or water-insoluble. Advantageously, water-insoluble resinous binders are used, in particular in combination with the preferred co-condensation products of diazonium salts. Examples of suitable binders are polyalkyl acrylates, methacrylic acid/alkyl methacrylate copolymers, polymers having lateral sulfonylurethane groups, phenolic resins, urea resins, melamine resins, epoxy resins, polyurethanes, polyvinyl esters and polyvinyl acetals.

The proportion of diazonium salt polycondensation product is in general 10 to 100, preferably 20 to 95, % by weight, and the amount of binder is 0 to 90, preferably 5 to 80, % by weight of the total layer.

The nature of the layer support depends on the intended use of the light-sensitive material. To produce planographic printing plates, aluminum which preferably carries an anodically produced porous oxide layer is generally employed. The aluminum is advantageously roughened mechanically, chemically or electrolytically before the anodizing. The anodizing is carried out in a known manner, for example in sulfuric acid and/or phosphoric acid, preferably under conditions which are such that an oxide layer weighing about 0.5 to 10 g/m² is obtained.

Before applying the light-sensitive layer, the

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oxide layer is advantageously subjected to a pretreatment to improve the printing characteristics, especially the hydrophilic character, for example a pretreatment with silicates, polyvinylphosphonic acid, hexafluorozirconates, heteropoly acids, tetraalkyl titanates or polyacrylic acids. The coating of the support is carried out in a known manner by spin-coating, spraying or dipping, or by means of rolls or slot dies, or by doctor application or casting.

10 Not only aluminum, but also steel, zinc, copper, chromium-plated steel or chromium-plated copper, plastic films, for example of polyethylene terephthalate or cellulose acetate, or screen-printing supports, for example Perlon gauze or nickel screens, can be used.

15 The process according to the invention is preferably used for the production of planographic printing forms. It can also serve for the production of gravure printing forms, letterpress and in particular flexographic printing forms, screen printing stencils, etch resists and
20 electroplating resists.

The imaging of the copying materials is carried out in a known manner, for example by contact exposure under a transparent original. For this, the customary light sources, such as carbon arc lamps, xenon lamps, metal halide-modified mercury high pressure lamps and the like, are used.

The imaging can also advantageously be effected with laser light, for example with an argon ion laser. With this type of exposure, a particularly great increase

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in the exposure effectiveness is achieved by the process according to the invention.

Within the scope of the present process, actinic light is generally suitable for image exposure, ie. radiation in the region of the near ultraviolet and of short-wave visible light.

The development of the exposed and warmed copying materials is effected in a known manner by washing out the unexposed areas of the layer with a developer. The composition of the developer depends on the nature and solubility of the light-sensitive layer. Suitable developers are organic solvents or solvent mixtures, water, which can contain small amounts of organic solvents or wetting agents, and, in particular, alkaline or weakly acidic aqueous solutions, which can contain buffer salts, neutral salts, organic solvents, wetting agents, dyestuffs and other customary additives. Developers which are free from organic solvents are preferred.

The invention has the effect that the hardening of the exposed layer areas is increased to such a degree that the exposure time can be reduced to about half that which is required without ultrasonic treatment. In the case of laser irradiation, even greater differences can be achieved. As an additional effect of the ultrasonic treatment, distinctly better in-depth hardening of the exposed areas of the layer occurs. Furthermore, screen areas are developed more cleanly throughout, continuous-tone wedge edges become sharper, and uncrosslinked parts of the layer are developed more rapidly. This advantage particularly manifests itself

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in the production of printing plates, especially planographic printing plates, where printing is to be effected from the hardened image layer.

The examples which follow illustrate the invention.

- 5 Parts by weight (p.b.w.) and parts by volume (p.b.v.) are related in the same way as g is related to ml. Percentage data and quantity ratios are to be understood as being in weight units, unless stated otherwise.

Example 1

- 10 Electrochemically roughened and anodized aluminum, bearing an oxide layer of 3 g/m^2 , which had been pre-treated with an 0.1% strength aqueous solution of polyvinylphosphonic acid, was used as the layer support for printing plates. The support was coated with a solution of the
- 15 following composition: 11.7 p.b.w. of a 34.7% strength solution of a methyl methacrylate/methacrylic acid copolymer having an acid number of 110 and a mean molecular weight of 35,000, in methyl ethyl ketone, 2.0 p.b.w. of the dimethyl ester of hepta-1,6-diene-2,6-dicarboxylic
- 20 acid, 2.0 p.b.w. of trimethylolethane triacrylate, 0.07 p.b.w. of 9-phenylacridine, 0.07 p.b.w. of 4-dimethylamino-4'-methyldibenzalacetone, 0.04 p.b.w. of an azo dyestuff obtained from 2,4-dinitro-6-chlorobenzenediazonium salt and 2-methoxy-5-acetylamino-N-cyanoethyl-N-hydroxyethyl-
- 25 aniline, 38.0 p.b.w. of ethylene glycol monoethyl ether and 13.5 p.b.w. of butyl acetate.

The mixture was applied by spin-coating, in such a way as to give a dry weight of $2.8 - 3 \text{ g/m}^2$. The plate was then dried for 2 minutes at 100°C in a circulat-

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ing air drying oven.

The light-sensitive coated plate was coated with a 15% strength aqueous solution of polyvinyl alcohol (12% of residual acetyl groups, K value 4). After drying, a covering layer weighing 4-5 g/m² was obtained.

The printing plate obtained was exposed for 30 seconds using a 5 kW metal halide lamp at a distance of 110 cm, under a 13 step exposure wedge having density increments of 0.15.

The exposed plate was cut in half. One half was developed immediately and the other half was passed through a commercial ultrasonic apparatus (USIG 1500 from Messrs. Schoeller Schall, Frankfurt, 15-21 kHz, 1500 W), the waterbath of which was warmed to 25°C. The residence time of the plate in the apparatus was 10 minutes.

Thereafter, both halves of the plate were developed in a developer of the following composition: 120 p.b.w. of sodium metasilicate x 9 H₂O, 2.13 p.b.w. of strontium chloride, 1.2 p.b.w. of a non-ionic wetting agent (coconut fatty alcohol polyoxyethylene ether, containing about 8 oxyethylene units), 0.12 p.b.w. of an anti-foam agent and 4,000 p.b.w. of fully demineralized water.

The plate was acidified with 1% strength phosphoric acid and inked with a greasy printing ink. The following completely crosslinked wedge steps were obtained:

with
ultrasonic treatment

6

without
ultrasonic treatment

4

The printing plate which had been subjected to an

ultrasonic treatment before development had a life of 210,000 prints, while the plate which had not been so treated had a life of 190,000 prints.

Example 2

5 The layer support specified in Example 1 was spin-coated with a solution of the following composition, so as to give a coating weight of 3 g/m²: 11.7 p.b.w. of the copolymer solution specified in Example 1, 38.0 p.b.w. of ethylene glycol monoethyl ether, 13.5 p.b.w. of butyl acetate, 3.9 p.b.w. of the diethyl ester of hepta-1,6-
10 diene-2,6-dicarboxylic acid, 0.07 p.b.w. of 9-phenylacridine, 0.04 p.b.w. of the azo dyestuff specified in Example 1 and 0.07 p.b.w. of 4-dimethylamino-4'-methyl-dibenzalacetone.

15 The plate was processed further in the same manner as in Example 1.

The following number of completely crosslinked wedge steps was obtained:

	<u>Ultrasonic treatment</u> <u>(5 minutes at 38°C)</u>	<u>Without</u> <u>ultrasonic treatment</u>
20	7	5

A printing trial was carried out. For this purpose, an offset printing plate, inked with a greasy ink, was clamped into a commercial printing machine (Heidelberg type GT0). After 200,000 prints, the printing trial
25 was discontinued, even though no breaking-off was observable in the 60-line/cm screen.

Comparable results were obtained when, in place of 9-phenylacridine, 2,2-dimethoxy-2-phenylacetophenone or

2-(4-ethoxynaphth-1-yl)-4,6-bis-trichloromethyl-s-triazine or 2-(acenaphth-5-yl)-4,6-bis-trichloromethyl-s-triazine was used.

Example 3

- 5 The layer support specified in Example 1 was spin-coated with a solution of the following composition, so as to give a coating weight of 3.5 g/m²: 10.0 p.b.w. of a 21.7% strength solution of a terpolymer of styrene, n-hexyl methacrylate and methacrylic acid
- 10 (10:60:30), having an acid number of 190, in butanone, 2.0 p.b.w. of trimethylolethane triacrylate, 0.06 p.b.w. of 9-phenylacridine and 0.03 p.b.w. of methyl violet (C.I. 42,535) in 18.0 p.b.w. of butanone and 7.5 p.b.w. of butyl acetate.
- 15 The coated plate was then dried for 2 minutes at 100°C in a circulating air drying oven, and was provided with a covering layer as in Example 1. The plate was exposed under a 13 step exposure wedge, as described in Example 1, for 4, 8, 15 and 30 seconds, and was developed
- 20 with a developer of the following composition: 5.3 p.b.w. of sodium metasilicate x 9H₂O, 3.4 p.b.w. of tert.-sodium phosphate x 12 H₂O, 0.3 p.b.w. of sec.-sodium phosphate and 91.0 p.b.w. of fully demineralized water.

- 25 In parallel, a plate was produced and exposed in the same way, but directly after exposure it was subjected to an ultrasonic treatment for 15 minutes in water at 22°C in the ultrasonic apparatus specified in Example 1. The plates were acidified with 1% strength phosphoric acid and inked with a greasy printing ink. Counting the completely

crosslinked gloss steps gave the following picture:

Exposure time:		S e c o n d s			
5 kW MH lamp		4	8	15	30
5	corresponding without*)	0	1	3	5
	completely with *)	1	3	5	7
crosslinked					
gloss steps					

*) Ultrasonic treatment for 15 minutes in water at 22°C

Example 4

- 10 A printing plate produced as described in Example 3 was exposed for 30 seconds under a 13 step continuous-tone step wedge. 5 wedge steps were obtained. Another corresponding plate was exposed for 15 seconds and then subjected to ultrasonic treatment for 5 minutes. Both plates gave
- 15 5 hardened wedge steps.

The plates were then used for printing on a commercial printing machine (Heidelberger GTO). The plate which had not been subjected to ultrasonic treatment showed signs of wear after only 150,000 prints, while the plate which had

20 been subjected to ultrasonic treatment showed signs of wear only after 180,000 prints.

Example 5

- The layer support specified in Example 1 was spin-coated with a solution of the following composition,
- 25 so as to give a coating weight of 3.5 g/m²: 2.6 p.b.w. of the diethyl ester of hepta-1,6-diene-2,6-dicarboxylic acid, 6.5 p.b.w. of a styrene/maleic acid ester copolymer having an acid number of 145-160 and a softening point of

140-160°C, 70.0 p.b.w. of ethylene glycol monomethyl ether, 0.1 p.b.w. of 9-phenylacridine, 0.035 p.b.w. of the azo dyestuff specified in Example 1 and 1.0 p.b.w. of the reaction product obtained from 1 mole of 2,2,4-trimethyl-
5 hexamethylene diisocyanate and 2 moles of 2-hydroxyethyl methacrylate.

The coated plate was then dried for 2 minutes at 100°C in a circulating air drying oven and provided with a covering layer as in Example 1. The plate was ir-
10 radiated with 200 mW and 1200 L/inch = 5.3 mJ/cm² in a Laserite^(R) 150 R apparatus, equipped with an argon ion laser, from Messrs. Eocom Corp. After irradiation, the image contrast was good. The plate was then developed with the developer of Example 1. The number of completely
15 crosslinked wedge steps of a continuous-tone step wedge was 3, in the case of exposure followed immediately by development.

7 wedge steps were obtained when an identical plate was processed in an identical manner, with the
20 difference that between exposure and development it was subjected to ultrasonic treatment for 10 minutes in water at 20°C in an ultrasonic apparatus.

If, after exposure, 1 hour was allowed to pass and the plate was then subjected to ultrasonic treat-
25 ment and thereafter developed, likewise 7 wedge steps are obtained.

The proof printing and production printing were effected on a Heidelberg GTO offset printing machine with an alcoholic fountain solution, and 150,000 sheets

24

were obtained. In the case of the plate which had been subjected to ultrasonic treatment the run increased to 170,000 sheets.

Example 6

- 5 a) An electrochemically roughened and anodized aluminum surface bearing an oxide layer of 3 g/m^2 was spin-coated with a solution of the following composition, so as to give a layer weighing 3 g/m^2 : 11.4 p.b.w. of the copolymer solution specified in Example 1, 37.9 p.b.w. of ethylene glycol monoethyl ether, 13.45 p.b.w. of butyl acetate, 4.0 p.b.w. of trimethylolethane triacrylate, 0.07 p.b.w. of 4-methylbenzalquinaldine, 0.08 p.b.w. of the azo dyestuff specified in Example 1, 0.07 p.b.w. of 4-dimethylamino-4'-methyldibenzalacetone and 0.56 p.b.w. of bis-undecyl disulfide.

The coated plate was dried for 2 minutes at 100°C in a drying oven.

- b) A further plate was produced in the same manner and was provided with a covering layer of $4\text{--}5 \text{ g/m}^2$ of poly-
20 vinyl alcohol, as in Example 1.
- c) A third plate was prepared as under a), but without addition of bis-undecyl disulfide.
- d) A fourth plate was prepared as under c) and was provided with a covering layer according to b).

- 25 Samples of the offset printing plates obtained were exposed, by means of a 5 kW metal halide lamp, for 10, 20 and 40 seconds under a 13 step exposure wedge having density increments of 0.15.

One half of each of the plates described under a)

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to d) was passed directly after exposure through the ultrasonic apparatus specified in Example 1. The temperature was 25°C, and the residence time was 50 seconds. In each case, the other half was not subjected to the ultrasonic treatment.

Thereafter, all the plates were developed with the developer described in Example 1.

The plates were then acidified with 1% strength phosphoric acid and inked with a greasy printing ink. The following number of completely crosslinked wedge steps was obtained:

15	Plate	Covering layer	Disulfide	<u>Exposure time (seconds)</u>					
				without ultrasonic treatment			with ultrasonic treatment		
				10	20	40	10	20	40
	a	-	+	-	1	3	-	1.5	3.5
	b	+	+	-	1	3	1	3	4
20	c	-	-	-	-	2	-	1	3
	d	+	-	-	1	3	1	3	4

Example 7

In order to demonstrate the broad applicability of the process, commercial photopolymerizable planographic printing plates (Lydel^(R) Ia, Du Pont, and XN, 3 M Co.) were exposed for 30 seconds under a continuous-tone wedge and then subjected to an ultrasonic treatment for 30 seconds. Thereafter, the plates were developed with the developers supplied by the manufacturers, in accordance with the instructions provided. Comparison samples without ultra-

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sonic treatment were developed directly.

The following wedge steps were obtained:

5	Exposure time (sec)	<u>Lydel Ia</u>		<u>XN</u>	
		without ultrasonic treatment	with ultrasonic treatment	without ultrasonic treatment	with ultrasonic treatment
	30	7	8	6	7

Example 8

A solution of 0.6 p.b.w. of the polycondensation
 10 product obtained from 1 mole of 3-methoxydiphenylamine-4-
 diazonium salt and 1 mole of 4,4'-bis-methoxymethyldiphenyl
 ether, the product being isolated as the mesitylene
 sulfonate, 0.05 p.b.w. of phosphoric acid, 0.27 p.b.w. of
 Hostaperm Blue B 2 G (C.I. 74,160), 1.87 p.b.w. of poly-
 15 vinylformal (Formvar 12/85) and 0.01 p.b.w. of methyl
 orange in 2.2 p.b.w. of ethylene glycol methyl ether
 acetate and 95 p.b.w. of ethylene glycol monomethyl ether
 was applied to the layer support specified in Example 1
 and dried for 4 minutes at 90°C.

20 A sample of the printing plate obtained was
 exposed for 40 seconds under a 13 step exposure wedge and
 then developed with a solution of 5.7 p.b.w. of $\text{MgSO}_4 \times$
 7 H_2O , 20.2 p.b.w. of n-propanol, 1 p.b.w. of ethylene
 glycol monobutyl ether and 0.7 p.b.w. of an ethoxylated
 25 alkylphenol in 72.4 p.b.w. of water. 5 completely
 crosslinked wedge steps were obtained.

A further sample of the same light-sensitive
 printing plate was exposed as specified above, but, after
 exposure, was subjected to ultrasonic treatment for 10
 30 minutes at 40°C. After development, 6-7 wedge steps were

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obtained.

Example 9

A solution of 7 p.b.w. of polyvinyl cinnamate, 12.5 p.b.w. of an epoxy resin having an epoxy equivalent weight of 365-420 (Araldite B), 2 p.b.w. of a hydrogenated rosin ester (Staybelite Ester 10), 0.07 p.b.w. of 2-benzoyl-methylene-1-methyl- β -naphthothiazoline and 10 p.b.w. of Renol Carmin FBB-H (C.I. 12,485) in 90 p.b.w. of ethylene glycol ethyl ether acetate was applied to an electro-chemically roughened and anodically oxidized aluminum plate, which was then dried for 3 minutes at 90°C. A part of the plate was exposed under a 13 step exposure wedge for 25 seconds and subsequently developed with a solution of 43 p.b.w. of ethylene glycol ethyl ether acetate, 21 p.b.w. of ethylene glycol monoethyl ether, 15 p.b.w. of an addition product of about 8-12 moles of ethylene oxide with tridecanol, 12.5 p.b.w. of butyrolactone, 4 p.b.w. of acetic acid, 3 p.b.w. of phosphoric acid and 0.3 p.b.w. of water. 7 hardened wedge steps were obtained.

20 A further sample of the light-sensitive printing plate was exposed as specified above, but was subjected to ultrasonic treatment for 60 seconds after exposure. After development, 9 hardened wedge steps were obtained.

Patent Claims

1. A process for the production of relief copies, in which process the light-hardenable layer of a light-hardenable copying material, which layer contains a photopolymerizable mixture, a photodimerizable polymeric compound or a diazonium salt polycondensation product, is exposed imagewise and thereafter the unexposed areas of the layer are washed out by means of a developer, characterized in that said process comprises subjecting the layer briefly to ultrasonic treatment after exposure, and then developing it.
2. The process as claimed in claim 1, wherein the layer is subjected to ultrasonic treatment at a temperature within the range of 4-50°C.
3. The process as claimed in claim 1, wherein the layer is subjected to ultrasonic treatment for 5 seconds up to 40 minutes.
4. The process as claimed in claim 1, wherein a light-hardenable copying material having a photopolymerizable layer is used, which layer contains a polymerizable compound having at least two terminal ethylenically unsaturated double bonds, a polymeric binder and a photo-initiator which, on exposure, is capable of generating free radicals.