

Our. Ref

298080

FORM 1

AUSTRALIA
Patents Act

614675

APPLICATION FOR A STANDARD PATENT

HOECHST AKTIENGESELLSCHAFT of 6230 Frankfurt/Main 80, Federal Republic of Germany

hereby applies for the grant of a standard patent for an invention entitled

Developing solvent for layers which are crosslinkable by
photopolymerization and process for the production of relief forms

which is described in the accompanying complete specification.

Details of basic application:

Country:

Application Number:

Application Date:

Federal Republic
of Germany

P 38 36 402.6

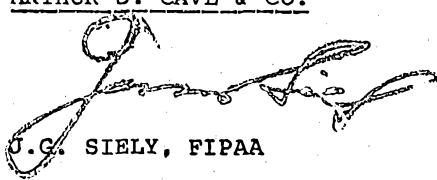
26 October 1988

The address for service is:

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SYDNEY NSW 2000

DATED this 24th day of October 1989

HOECHST AKTIENGESELLSCHAFT
By Its Patent Attorneys
ARTHUR S. CAVE & CO.


J.G. SIELY, FIPAA

TO:

The Commissioner of Patents
COMMONWEALTH OF AUSTRALIA

FEE:

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PATENT DECLARATION FORM (CONVENTION)

COMMONWEALTH OF AUSTRALIA

Patents Act 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION
FOR A PATENT

In support of the Convention application made for a patent for an invention entitled: DEVELOPING SOLVENT FOR LAYERS WHICH ARE CROSSLINKABLE BY PHOTOPOLYMERIZATION AND PROCESS FOR THE PRODUCTION OF RELIEF FORMS

I, HECTOR JOHN CUMMING, Patent Attorney
of Level 10, 10 Barrack Street, Sydney, NSW, 2000, Australia
do solemnly and sincerely declare as follows:-

1. I am authorised by HOECHST AKTIENGESELLSCHAFT the applicant for the patent to make this declaration on its behalf.
2. The basic Application as defined by Section 141 of the Act was made in the following country or countries on the following date namely:-
in FEDERAL REPUBLIC OF GERMANY on 26 October 1988 by HOECHST AKTIENGESELLSCHAFT
3. 1) Hans-Joachim SCHLOSSER, 2) GUENTHER SCHOEN
of 1) Am Rosengarten 2a, 6200 Wiesbaden/Bundesrepublik Deutschland
2) Friedrichstrasse 39, 6200 Wiesbaden/Bundesrepublik Deutschland
are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:

The Applicant is the Assignee of the said invention from the actual inventors.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

Declared at SYDNEY this 21st day of June, 1991.

To:

The Commissioner of Patents

ARTHUR S. CAVE & CO.
PATENT AND TRADE MARK ATTORNEYS
SYDNEY

Hector Cumming
HECTOR JOHN CUMMING F.I.P.A.A.

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- (54) Title
DEVELOPING SOLVENT FOR LAYERS WHICH ARE CROSSLINKABLE BY
PHOTOPOLYMERIZATION AND PROCESS FOR THE PRODUCTION OF RELIEF FORMS
- International Patent Classification(s)
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- (71) Applicant(s)
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ARTHUR S CAVE & CO, GPO Box 3876, SYDNEY NSW 2001
- (57) Claim

1. A process for the production of photopolymerization-crosslinked relief forms, which comprises the steps of imagewise exposing to actinic light a layer which is crosslinkable by photopolymerization and contains a binder based on an elastomeric polymer, a photopolymerizable monomer compatible therewith and a photoinitiator, and washing off the non-crosslinked portions of said layer with a developing solvent comprising an ester of the general formula I



wherein

R^1 and R^2 are the same or different and denote $(\text{C}_1\text{-C}_{13})\text{n-alkyl}$ or iso-alkyl , C_5 , C_6 or $\text{C}_{12}\text{-cycloalkyl}$, $(\text{C}_1\text{-C}_3)\text{alk-C}_6\text{-aryl}$, C_6 or $\text{C}_{10}\text{-aryl}$, provided that the sum of carbon atoms in R^1 and R^2 is from 6 to 13.

4. A process as recited in claim 1, wherein said solvent contains from about 55 to 90% by weight of said ester and about 45 to 10% of an alcohol.

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FORM 10

COMPLETE SPECIFICATION

(ORIGINAL)

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority:
Related Art:

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Complete specification for the invention entitled

"Developing solvent for layers which are
crosslinkable by photopolymerization and process
for the production of relief forms".

The following statement is a full description of this invention, including the
best method of performing it known to me:-

DEVELOPING SOLVENT FOR LAYERS WHICH ARE CROSSLINKABLE BY
PHOTOPOLYMERIZATION AND PROCESS FOR THE PRODUCTION
OF RELIEF FORMS

Background of the Invention

5 The invention relates to a developing solvent
for layers which are crosslinkable by
photopolymerization and contain a binder based on an
elastomeric polymer, a photopolymerizable monomer
compatible therewith and a photoinitiator.

10 It has long been known to produce relief
forms, in particular flexographic printing plates,
by means of photopolymerization-crosslinkable layers
which are exposed imagewise and thereafter developed
and washed out.

15 For the production of these forms, the
photopolymer layer is exposed imagewise to actinic
light; a relief can then be formed by washing off
the non-exposed and thus non-crosslinked portions of
the layer, using a developing solvent. The
20 developing solvent should dissolve the non-
crosslinked portions of the layer as quickly as
possible, and the solvent must be removable with

greatest possible ease from the crosslinked portions of the layer, so that the plate is rapidly dried.

For this reason, low-boiling developing solvents presently are generally used.

5 Examples of preferred solvents which are described in DE-A 22 15 090 include methyl ethyl ketone, benzene, toluene, xylene, carbon tetrachloride, trichloroethane, tri-chloroethylene, methyl chloroform and tetrachloroethane, and
10 mixtures of these.

15 It is a disadvantage of the above-indicated chlorinated hydrocarbons that they are toxic and give rise to disposal problems. If chlorinated hydrocarbons are used as developing solvents, the portions of the layer which are to be removed swell very strongly while still on the plate and as the concentration of dissolved components of the non-crosslinked layer portions increases in the developing solvent, viscosity of the solvent rises sharply. As a result, the capacity of the
20 developing solvent is very limited and the solvent is rendered useless, already at a solids content of 5%. A further consequence of the strong increase in viscosity is that plates develop very slowly even
25 at less than 5% solids content. Of the non-chlorinated hydrocarbons specified in DE-A 22 15 090 benzene, toluene and xylene are mentioned. These solvents have the disadvantage of being easily flammable, moreover, they lead to severe swelling
30 of the layer and, consequently, to slow developing and drying of the plate. Additionally, due to their

low flash-point, these solvents cannot be used in developing apparatuses which are not explosion-proof.

5 DE-A 36 00 116 describes relatively highly boiling developing solvents which contain hydrocarbons, alcohols or ketones which are branched, or cyclic with one or three olefinic double bonds, or saturated, or cycloaliphatic with one to three olefinic double bonds. Monoterpenes
10 are mentioned in particular. Limonene which is used in the example may have good developing characteristics, but is sensitive to oxygen and irritates the skin, properties which should not be present in a developing solvent. It is also a
15 disadvantage of limonene that it permits only very slow development and is difficult to remove from the layer.

Summary of the Invention

20 It is therefore an object of the present invention to provide a developing solvent for photopolymer layers, which

- is non-toxic,
- has a high flash-point,
- can be removed from the layer as
25 completely and quickly as possible, without giving rise to swelling of the layer and
- shows the smallest possible increase in viscosity when taking up components of

the layer, so that it is possible to develop quickly and faultlessly, irrespective of high capacity requirements.

It is also an object of the invention to provide a process for the production of photopolymerization-crosslinked relief forms which employs the developing solvent according to the present invention.

In accomplishing these objects there has been provided a developing solvent, comprising, an ester of the general formula I



wherein

R^1 and R^2 are the same or different and denote $(\text{C}_1 - \text{C}_{13})$ n-alkyl or iso-alkyl, C_3 , C_6 or C_{12} -cycloalkyl, $(\text{C}_1 - \text{C}_3)$ alk- C_6 -aryl, C_6 or C_{10} -aryl, provided that the sum of carbon atoms in R^1 and R^2 is from 6 to 13.

Further objects, features and advantages of the present invention will become apparent from the detailed description of preferred embodiments that follows.

Detailed Description of the Preferred Embodiments

Preference is given to those esters of the general formula I, in which the sum of carbon atoms in R^1 and R^2 is from 6 to 10.

5 Particularly preferred are esters of the general formula I, in which

R^1 denotes $(C_1-C_{13})n$ -alkyl, in particular $(C_1-C_5)n$ -alkyl, C_{12} -cycloalkyl, alkaryl, in particular benzyl or phenyl, and

10 R^2 denotes $(C_3-C_9)n$ -alkyl or iso-alkyl, provided that R^1 does not stand for alkaryl or phenyl, $(C_1-C_4)n$ -alkyl or iso-alkyl, in particular $(C_1-C_4)n$ -alkyl, provided that R^1 is benzyl or phenyl and benzyl or phenyl, provided that R^1 is $(C_1-C_5)n$ -alkyl or (C_1-C_5) iso-alkyl.

15 Examples of particularly preferred esters corresponding to the general formula I are:

20 Amyl acetate, isoamyl acetate, hexyl acetate, cyclohexyl acetate, ethylhexyl acetate, nonyl acetate, isononyl acetate, propyl propionate, propyl butyrate, butyl butyrate, isobutyl butyrate, benzyl acetate, methyl benzoate.

25 The esters of the general formula I may be contained in the developing solvent of the present invention, either individually or in the form of a mixture of various esters corresponding to the general formula I. Preferred are developing solvents which contain only one ester of the general formula I.

The developing solvent according to the invention comprises from about 55 to 100% by weight, particularly from about 55 to 90% by weight, of ester of the general formula I.

5 Apart from the esters of the general formula I, the developing solvent of this invention may contain other solvents as additions, particularly if the polymer layer carries an additional polyamide-containing protective layer. In this
10 event, alcohols, especially relatively highly boiling alcohols, are preferred for use as additional solvents.

15 The principal constituents of the photopolymerization-crosslinkable layers which are to be developed using the developing solvent of the present invention comprise a binder based on an elastomeric polymer, a photopolymerizable monomer which is compatible with the binder, and a photoinitiator. The layers may also comprise
20 various binders, monomers or photoinitiators.

25 Additions which may be contained in the layers include dyes, pigments, anti-halation agents, antioxidants, plasticizers, antiozonants, crosslinking agents, regulators, fillers, levelling agents and other agents which improve the action of the layers.

30 Further auxiliary agents which may be added to the above-described layer are, for example, inhibitors to prevent thermal polymerization, such as hydroquinone and its derivatives, 2,6-di-tert.-butyl-p-cresol, nitrophenols, nitrosamines, such as

N-nitrosodiphenylamine, or salts of N-nitrosocyclohexylhydroxylamine, e.g., the alkali metal or aluminum salts thereof.

5 Particularly preferred layers which are crosslinkable by photopolymerization are those which contain binders comprising polymers of conjugated aliphatic dienes, the monomer units of which have 4 to 5 carbon atoms. Among these the following are particularly mentioned: natural rubber, homo-
10 polymers of butadiene and isoprene, copolymers of butadiene and isoprene, copolymers of butadiene and/or isoprene with other monomers, such as styrene, vinyl toluene, acrylonitrile, or (meth)acrylic alkyl esters, for example, nitrile
15 rubbers according to EP-A 064 564, random copolymers of styrene/butadiene, styrene/isoprene, and styrene/isoprene/butadiene, or block polymers of styrene monomers and butadiene and/or isoprene having a styrene content of about 10 to 50% by
20 weight. Elastomers of this kind are described in DE-B 22 15 090, DE-A 24 56 439, DE-A 29 42 183, and DE-A 21 38 582.

The layers which are crosslinkable by photopolymerization generally contain from about 20
25 to 95% by weight, preferably from about 30 to 95% by weight, of binder.

Preferred monomers having one or more polymerizable olefinic double bonds are, in particular, esters and amides of acrylic and
30 methacrylic acid. Examples are the compatible mono and diacrylates and mono and dimethacrylates of

monohydric or polyhydric alcohols, such as ethylene glycol, di-, tri-, tetra- or polyethylene glycols, the latter preferably having from about 10 to 15 ethylene glycol units, 1,3- propane diol, 1,6-hexane diol, dodecane diol, glycerol, 1,1,1-trimethylol propane, 1,2,4-butanetriol, or pentaerythritol, for example, ethylene glycol monomethacrylate, 1,3-propanediol monomethacrylate, hexanediol diacrylate, hexanediol dimethacrylate, 2-ethyl-hexylacrylate, lauryl methacrylate, stearyl methacrylate, glycerol mono or diacrylate, 1,2,4-butanetriol monomethacrylate, pentaerythritol triacrylate, polyethylene glycol methyl ether acrylate, tetradecaethylene glycol dimethacrylate or the triether of glycerol and 3 mols of N-methylol acrylamide or methacrylamide. The amount of monomers contained in the layer is, in general, from about 1 to 70% by weight, preferably from about 2 to 50% by weight, of the non-volatile constituents of the composition.

Photoinitiators which can be used are the known compounds which exhibit sufficient thermal stability in the processing of recording materials and which form a sufficient number of free radicals, when exposing and thereby initiating polymerization of the monomers. The photoinitiators should absorb light in the wavelength region from about 250 to 500 nm, forming radicals in the process. Examples of preferred photoinitiators are acyloins and the derivatives thereof, such as benzoin, benzoin alkylethers, for example, benzoin isopropyl ether,

vicinal diketones and the derivatives thereof, for example, benzil, benzil acetals such as benzil dimethyl ketal, fluorenones, thioxanthenes, polynuclear quinones, acridines and quinoxalines; and also trichloromethyl-s-triazines, 2-halo-methyl-4-vinyl-1,3,4-oxadiazole derivatives, halogen-containing oxazoles substituted by trichloromethyl groups, carbonyl methylene heterocycles containing trihalomethyl groups, according to DE-A 33 33 450, acyl phosphine oxide compounds as described, for example, in DE-A 31 33 419 and other phosphorus - containing photoinitiators, for example, the 6-acyl-(6H)-dibenz-[c,e]-[1,2]-oxaphosphorin-6-oxides, in particular 6-(2,4,6-trimethylbenzoyl)-(6H)-dibenz-[c,e][1,2]-oxaphosphorin-6-oxide described in German patent application P 38 27 735.2. The photoinitiators can also be used in combination with one another or with coinitiators or activators, respectively, for example, with Michler's ketone and its derivatives or with 2-alkyl anthraquinones.

The amount of photoinitiator is, in general, from about 0.01 to 10% by weight, preferably from about 0.5 to 5% by weight, of the layer.

The compositions which are crosslinkable by photopolymerization can be used for the preparation of relief and flexographic printing plates by way of casting from a solution or extruding and calendering to form layers having a thickness of about 0.02 to 10 mm, preferably about 0.2 to 6 mm. The layer can be laminated to the surface of an appropriate

support or a solution of the composition can be applied to a layer support.

5 The above-indicated layers are not only used for the production of relief printing plates, but also for the production of, for example, planographic printing plates, gravure cylinders, screen printing stencils, and photoresists. Depending on the intended application, suitable supports comprise, for example, polyester films, steel or
10 aluminum sheets, copper cylinders, supports for screen printing stencils, foam layers, rubber-elastic supports, or circuit boards. It may also be advantageous to apply a covering or protective layer, for example, a thin layer of polyvinyl alcohol or polyamide, or a peelable covering film,
15 for example, of polyethylene terephthalate, to the photosensitive recording layer. Moreover, precoating of the support may be advantageous. The additional layer between the support and the
20 photosensitive layer may act, for example, as an anti-halation layer or as an adhesive layer.

The invention also relates to a process for the production of photopolymerization-crosslinked relief forms. In the process, the layers which are
25 crosslinkable by photopolymerization are imagewise exposed to the actinic light of light sources such as mercury vapor lamps or fluorescent tubes, the emitted wavelength ranging between about 230 and 450 nm, preferably between about 300 and 420 nm. The
30 non-exposed and thus non-crosslinked portions of the layer are removed with the aid of the developing

solvent according to the present invention, by spraying, washing or brushing. The developed relief forms are appropriately dried at temperatures up to about 120°C and may be post-exposed to actinic light, either simultaneously or subsequently.

The photopolymerization-crosslinked relief forms according to the invention are advantageously used in the production of printing forms, especially letterpress and relief printing forms, which are particularly suitable for flexographic printing. The invention is explained by the examples below.

Example 1

A commercial flexographic printing plate based on a styrene-isoprene-styrene three-block polymer (®Cyrel HL) as an elastomer having a layer thickness of 2.8 mm was first subjected to overall exposure from the back for 76 seconds, using a commercial fluorescent-tube exposure apparatus and thereafter exposed imagewise for 12 minutes, through a negative transparency placed in contact with it. After removing the covering layer, the exposed plate was developed in a commercial developing apparatus equipped with brushes, using hexyl acetate containing 15% by weight butanol. A washing off time of 5 minutes yielded the best results.

The flexographic printing form was dried for 1 hour at 50°C and stored for 15 hours at room temperature. Following a conventional post-treatment with an aqueous bromine solution, a

flexographic printing form of excellent quality was obtained.

Example 2

5 A commercial plate corresponding to Example
1 was exposed overall from the back for 76 seconds
and thereafter exposed for 12 minutes from the front
without using a negative transparency. After
removing the covering layer, the plate (diameter 50
10 mm) was placed for 10 minutes in 50 ml of hexyl
acetate. It was then wiped, dried for 1 hour at
50°C and stored for 17 hours. After storage, an
increase in weight of the plate of only 0.42% could
be determined, which was due to non-evaporated
developing solvent.

15 Example 3

The procedure of Example 2 was followed, but
the developing solvent used was cyclohexyl acetate.
The increase in weight of the plate after drying and
storage was 1.4%.

20 Example 4

The procedure of Example 2 was followed, with
the exception that butyl butyrate was used as the
developing solvent. The increase in weight of the
plate after drying and storage was only 1.05%.

Example 5 (Comparative Example)

A commercial plate as in Example 2 was processed in accordance with the instruction given in Example 2, with the exception that xylene was used as the developing solvent. The increase in weight of the plate after drying and storage under the conditions indicated in Example 2 was, however, 1.92%. This means that a relatively large proportion of the solvent was still present in the plate.

Example 6 (Comparative Example)

A commercial plate was treated as described in Example 2. However, the developing solvent used was limonene. The increase in weight of the plate after drying and storage was 1.92%.

Example 7

To determine the capability (capacity) of developing solvents to take up components from non-crosslinked regions of a styrene-isoprene-styrene three-block polymer (®Cyrel HL), the viscosities of the corresponding developing solvents were measured at specific solids contents produced by components from the layer after development thereof. Table 1 shows the viscosity values determined in an Ubbelohde viscometer at 25°C, for solids contents of 5, 7.5 and 10% by weight.

Although the developing solvents of the present invention still exhibited a viscosity which allowed a very high developing speed at a solids content of 7.5% by weight, viscosity of perchloroethylene at a solids content of only 5% by weight was already so high that rapid development was no longer ensured.

Table 1

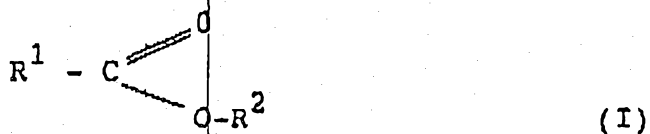
Developing Solvent	Viscosities [cSt] at Different Solids Contents [% by weight]		
	5	7.5	10
butyl butyrate	9.1	22	40.6
hexyl acetate	13	28	68
perchloroethylene	37.1	120.8	333.5

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- 15 -

The claims defining the invention are as follows:

1. A process for the production of photopolymerization-crosslinked relief forms, which comprises the steps of imagewise exposing to actinic light a layer which is crosslinkable by photopolymerization and contains a binder based on an elastomeric polymer, a photopolymerizable monomer compatible therewith and a photoinitiator, and washing off the non-crosslinked portions of said layer with a developing solvent comprising an ester of the general formula I



wherein

R^1 and R^2 are the same or different and denote $(\text{C}_1\text{-C}_{13})\text{n-alkyl}$ or iso-alkyl , C_5 , C_6 or $\text{C}_{12}\text{-cycloalkyl}$, $(\text{C}_1\text{-C}_3)\text{alk-C}_6\text{-aryl}$, C_6 or $\text{C}_{10}\text{-aryl}$, provided that the sum of carbon atoms in R^1 and R^2 is from 6 to 13.

2. A process as recited in claim 1, further comprising the steps of, drying at temperatures of up to about 120°C said relief form, and simultaneously or subsequently post-exposing said relief form to actinic light.

3. A process as recited in claim 1, wherein said solvent contains from about 55 to 100% by weight of said ester, and about 45 to 0% of an alcohol.

4. A process as recited in claim 1, wherein said solvent contains from about 55 to 90% by weight of said ester and about 45 to 10% of an alcohol.

5. A process as recited in claim 3 or 4 wherein the said alcohol is a relatively highly boiling alcohol.

DATED this 21st day of August, 1991.

HOECHST
AKTIENGESELLSCHAFT
By Its Patent Attorneys
ARTHUR S. CAVE & CO.