

The present invention relates to bis-4,6-trichloromethyl-s-triazines which in their 2-position are substituted by an aromatic group, and to a light-sensitive mixture containing these compounds.

Compounds of the above mentioned type are known as initiators for a number of photochemical reactions. They are employed, on the one hand, to utilize the free radicals formed under the action of actinic radiation for triggering polymerization reactions or color changes and, on the other hand, to initiate secondary reactions caused by the freed acid.

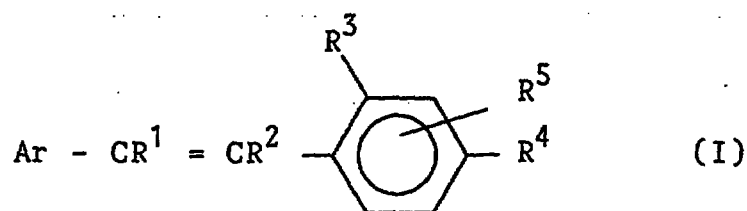
DE-A 22 43 621 describes styryl-substituted trichloromethyl-s-triazines exhibiting a number of advantageous properties. However, a disadvantage is presented by their relatively complicated manufacture.

DE-A 27 18 259 discloses 2-aryl-4,6-bis-trichloromethyl-s-triazines with polynuclear aryl groups, which have comparably good properties, in particular, a high sensitivity to light and which can be produced by simple methods. In general, however, they show this high sensitivity in one spectral range only, and, therefore, they cannot be processed into light-sensitive materials which are of the same high sensitivity to various light sources, for example argon ion lasers and gallium-doped mercury vapor lamps.

It has also been tried to combine photopolymerization initiators of other chemical natures with photopolymerization initiators containing trichloromethyl groups, in order to achieve different desired properties in one single mixture (DE-A 28 51 641).

It has been an object of the present invention to oppose photoinitiators which can be produced using simple methods, and the sensitivity of which to the UV radiation of an argon ion laser on the one hand and to the radiation of a gallium-doped mercury vapor high pressure lamp in the visible spectral range on the other hand is at least comparable to that of the photoinitiators which in the respective spectral ranges are particularly sensitive.

The instant invention relates to light-sensitive compounds of the general formula I



in which

R^1 and R^2 denote hydrogen atoms or methyl groups,

R^3 and R^4 are different from one another and each denote a hydrogen atom or a 4,6-bis-trichloromethyl-s-triazin-2-yl group,

R^5 denotes a hydrogen or halogen atom or an alkyl or alkoxy group, and

Ar is a phenyl group which may carry 1 to 3 substituents selected from the group including halogen atoms, alkyl, halogeno-alkyl, aralkyl, aryl-oxyalkyl, cycloalkyl, alkenyl, aryl or aryloxy groups, whereby in the alkyl groups individual methylene groups can be replaced by oxygen or sulphur atoms and two of these groups can each be linked to form a 5- or 6-member ring, and the maximum total number of carbon atoms contained in the substituents is 12;

or is a naphthyl, acenaphthyl, di- or tetrahydronaphthyl, indanyl, anthryl, phenanthryl, fluorenyl or tetrahydrophenanthryl group which can be substituted by halogen atoms, by alkyl groups having 1 to 3 carbon atoms, by alkoxy groups having 1 to 4 carbon atoms or by alkoxy-alkyl groups having 3 to 6 carbon atoms.

In accordance with this invention, there is furthermore proposed a light-sensitive mixture which contains a bis-trichloromethyl-s-triazine (a) and a compound (b) which is capable of reacting with the photoreaction product of the triazine (a) in such a way that a product is formed, the light absorption or solubility in developer of which is different from that of (b). The mixture according to this invention is characterized in that the triazine (a) is a compound of the above-defined formula I.

Under the action of actinic radiation, the compounds according to the invention form free radicals which are capable of initiating chemical reactions, in particular free-radical initiated polymerizations. When being irradiated, they also form hydrogen halide, by which acid-catalyzed reactions, such as, for example, splitting of acetal bonds or salt formation, such as color changes of indicator dyestuffs, can be initiated.

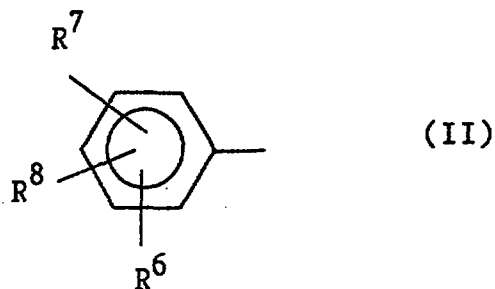
Within the scope of this specification, the term "actinic radiation" shall denote any radiation whose energy at least corresponds to that of short-wave visible light. Long-wave UV radiation is particularly suitable, but electron, x-ray or laser beams may also be used.

The symbols in the above general formula I preferably have the following meanings:

R^1 and R^2 denote hydrogen atoms,

R^5 denotes a hydrogen, chlorine or bromine atom, an alkyl group having 1 to 3 carbon atoms, or a methoxy group, and

Ar denotes a phenyl group of the general formula II



in which

R^6 to R^8 are identical or different and denote hydrogen atoms or one of the substituents listed above.

Particular preference is given to compounds of the general formula I wherein

R^1, R^2, R^3 , denote hydrogen atoms and
and R^5

Ar corresponds to general formula II, in which

R^6 to R^8 are identical or different and denote hydrogen, fluorine, chlorine or bromine atoms, alkyl, alkoxy or alkoxy-alkyl groups or

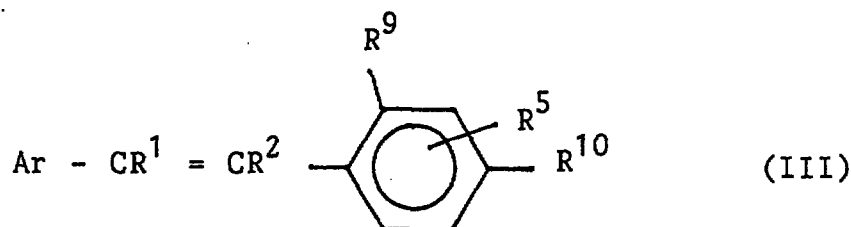
R^6 denotes a hydrogen atom and

R^7 and R^8 commonly denote a dioxymethylene group.

A compound which is very particularly preferred is 2-(4-styryl-phenyl)-4,6-bis-trichloromethyl-s-triazine.

Specific examples of particularly preferred compounds forming the Ar groups are: phenyl; 2-, 3- or 4-fluorophenyl; 2-, 3- or 4-chlorophenyl; 2-, 3- or 4-bromophenyl; 2-, 3- or 4-methyl, -ethyl, -propyl, -butyl, -isobutyl, -hexyl, -nonyl or -dodecyl phenyl; 2-, 3- or 4-methoxy, -ethoxy, -isopropoxy, -butoxy, -pentoxy, -octyloxy or -decyloxy phenyl; 2,4-dichloro- or -dibromophenyl; 3,4-dichloro- or -dibromophenyl; 2,6-dichlorophenyl; 3-bromo-4-fluorophenyl; 2,3-, 2,4-, 2,5-, 3,4- or 3,5-dimethoxy-, -diethoxy-, -dibutoxy- or -dihexoxy phenyl; 2-ethoxy-5-methoxy phenyl; 3-chloro-4-methyl phenyl; 2,4-dimethyl phenyl; 2-, 3- or 4-methoxyethyl, -ethoxyethyl or -butoxyethyl phenyl; 2,4,6-trimethyl phenyl; 3,4,5-trimethoxy or -triethoxy phenyl; 2,3-dioxymethylene phenyl; or 3,4-dioxymethylene phenyl.

The simplest and preferred way of producing the aryl-bis-trichloromethyl-s-triazines according to this invention is the co-trimerization of 1 mole of aryl carboxylic acid nitrile of the general formula III



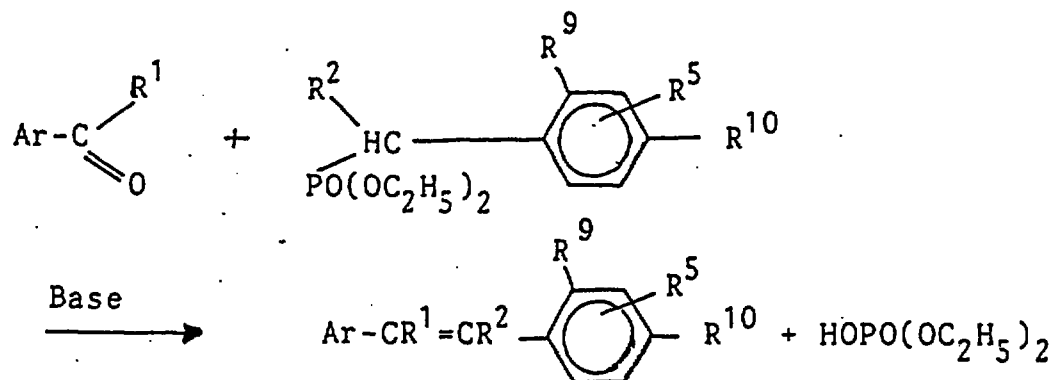
in which

R^9 and R^{10} are different from one another and each denote a hydrogen atom or a CN group, and

Ar, R^1 , R^2 and R^5 have the same meaning as in Claim 1,

and 2 - 8 moles of trichloroacetonitrile in the presence of hydrogen halide, preferably hydrogen chloride and Friedel-Crafts catalysts, such as $AlCl_3$, $AlBr_3$, $TiCl_4$ and borotrifluoride etherate, in analogy with the procedure described in the "Bull. Chem. Soc. Jap." 42, 2924 (1969). Other ways of performing the synthesis are reacting the aryl amidines with polychloro-3-aza-pent-3-ene in accordance with the method published in "Angew. Chemie" 78, 982 (1966) or, for example, reacting carboxylic acid chlorides or carboxylic acid anhydrides with N-(iminoacyl)-trichloroacetamidines; 2-aryl-4-methyl-6-trichloromethyl-s-triazines can also be easily prepared by the last-mentioned reaction, as is described in GB-A-912,112.

The nitriles employed for co-trimerization can be synthesized in a particularly simple way by a Horner-Wittig reaction (see "Houben-Weyl", vol. 5/1b, pp. 396-401 and 895-899) following the pattern



wherein R⁹ or R¹⁰ denotes the nitrile group and all other groups have the same meaning as in general formula I. The aralkylphosphonic acid diethyl ester is obtained, in a smooth reaction, by reacting the corresponding α-halo- genoalkyl aromatic compound with triethyl phosphite.

Of course, the nitriles can also be prepared by other methods which are known from literature, by exchange reactions or from the corresponding carboxylic acids or carboxylic acid derivatives. In "Methoden der organ. Chemie" (Methods of Organic Chemistry), (Houben-Weyl), vol. 5/1b (1972), a great number of syntheses of substituted stilbenes are described.

The novel compounds according to this invention are suitable as photoinitiators for photopolymerizable layers which contain, as essential constituents, monomers, binders and initiators.

Photopolymerizable monomers which can be employed for this purpose are known and are described, for example, in US-A Nos. 2,760,863 and 3,030,023.

Preferred examples are acrylic and methacrylic acid esters of polyhydric alcohols, such as diglycerol diacrylate, polyethylene glycol dimethacrylate, acrylates and methacrylates of trimethylol ethane, trimethylol propane and pentaerythritol, and of polyhydric alicyclic alcohols. Reaction products of diisocyanates with partial esters of polyhydric alcohols are also used advantageously. Monomers of this kind are described in DE-A Nos. 20 64 079, 23 61 041 and 28 22 190.

The proportion of monomers contained in the layer in general varies between 10 and 80, preferably 20 and 60, percent by weight.

A great number of soluble organic polymers may be employed as binders. Examples are: Polyamides, polyvinyl esters, polyvinyl acetals, polyvinyl ethers, epoxide resins, polyacrylic acid esters, polymethacrylic acid esters, polyesters, alkyd resins, polyacrylamide, polyvinyl alcohol, polyethylene oxide, polydimethyl acrylamide, polyvinyl pyrrolidone, polyvinylmethyl formamide, polyvinylmethyl acetamide and copolymers of the monomers which form the homopolymers enumerated.

Other possible binders are natural substances or modified natural substances, for example gelatin and cellulose ethers.

With particular advantage, those binders are used which are insoluble in water, but soluble or at least swellable in aqueous-alkaline solutions, since layers containing such binders can be developed with the preferably employed aqueous-alkaline developers. Binders of this type can, for example, contain the following groups: $-\text{COOH}$, $-\text{PO}_3\text{H}_2$, $-\text{SO}_3\text{H}$, $-\text{SO}_2\text{NH}-$, $-\text{SO}_2\text{NHSO}_2$ and $-\text{SO}_2\text{-NH-CO}-$.

Examples of these are: maleate resins, polymers of β -methacryloyloxy-ethyl N-(p-tolyl-sulfonyl)-carbamate and copolymers of these and similar monomers with other monomers, and also styrene/maleic acid anhydride copolymers. Copolymers of alkylmethacrylate and methacrylic acid and copolymers of methacrylic acid, alkylmethacrylates and methylmethacrylate and/or styrene, acrylonitrile, and the like, which are described in DE-A 20 64 080 and DE-A 23 63 806, are preferably used.

In general, the quantity of binder amounts to 20 to 90, preferably 40 to 80, percent by weight of the layer constituents.

Depending on their intended use and desired properties, the photopolymerizable mixtures may contain various additional substances. Examples of these are:

- inhibitors to prevent thermal polymerization of the monomers,
- hydrogen donors,
- substances modifying the imaging properties of layers of this type,
- dyes,

- colored and uncolored pigments,
- color formers,
- indicators or
- plasticizers.

The photopolymerizable mixture of this invention can be used in many fields of application, such as, for example, the production of safety glass, varnishes which are hardened by the action of light or corpuscular radiation, such as electron beams, dental fillings and, in particular, as a light-sensitive copying material in the field of reproduction. Examples of possible applications in this field are: copying layers for the photo-mechanical production of printing forms suitable for relief printing, lithographic printing, gravure printing, screen printing, of relief copies, for example, in the production of Braille books, of single copies, tanned images or pigment images. The mixtures may further be employed for the photomechanical production of etch resists, for example for name plates, printed circuits and chemical milling.

The mixture can be used industrially for the above mentioned applications as a liquid solution or dispersion, for example, a photoresist solution, which is applied by the consumer to an appropriate support, for example, for chemical milling, for the production of printed circuits, screen printing stencils, a.s.o. The mixture may also be present as a solid light-sensitive layer on a suitable support, i.e., as a storable, presensitized copying material, for example, for the production of printing forms. It can also be employed for the production of dry resists.

It is in general advantageous to substantially isolate the mixtures from the influence of atmospheric oxygen during the light polymerization. If the mixture is used in the form of thin copying layers, it is recommended to apply a suitable cover film which has a low permeability to oxygen. The cover film may be self-supporting and be removed from the copying layer prior to development. Polyester films, for example, are suitable for this purpose. The cover film may also consist of a material which dissolves in the developer liquid or which can be removed at least from the non-hardened areas during development. Examples of materials suitable for this purpose are, inter alia, waxes, polyvinyl alcohol, polyphosphates or sugars.

Layer supports which are suitable for copying materials prepared using the mixture of this invention include, for example, aluminum, steel, zinc, copper and plastic films, such as films of polyethylene terephthalate or cellulose acetate, and screen printing supports, such as perlon gauze.

In their capacity as photoinitiators, the radiation-sensitive compounds are effective in quantities as low as about 0.05 percent of the total solids content of the composition, and an increase of this quantity beyond 10 percent is not appropriate, as a rule. Preferably, concentrations between 0.3 and 7 percent are used.

Furthermore, the compounds according to this invention may be used in those radiation-sensitive compositions which under the action of acid catalysts formed during photolysis of the initiator undergo a change in their properties. In this connection, the cationic polymerization of systems containing vinyl ethers, N-vinyl compounds, such as N-vinyl-carbazole, or special acid-cleavable lactones is to be mentioned, without precluding, however, that in some of these systems free-radical-initiated reactions may also take place. Furthermore, amino plastics, such as urea/formaldehyde resins, melamine/formaldehyde resins, and other N-methylol compounds, and phenol/formaldehyde resins may be mentioned as compositions which can be hardened by acids. Although it is normal for epoxy resins to be hardened by Lewis acids or by such acids whose anions are less nucleophilic than chloride, i.e., than the anion of the acids formed during photolysis of the new photoinitiators, layers composed of epoxy resins and novolaks harden readily upon exposure in the presence of the compounds according to the invention.

Yet another advantageous property of the new photoinitiators according to the invention is their capability of causing color changes in dyed systems during photolysis; of inducing color formation from color precursors, e.g., leuco compounds, or of causing bathochromic color shift or deepening in mixtures containing cyanine, merocyanine, or styryl dye bases. Further, in mixtures such as those disclosed in DE-A 15 72 080, which

contain a dye base, N-vinyl carbazole, and a halogenated hydrocarbon, the halogen compound tetrabromomethane may be replaced by a small percentage, i.e., about 2 %, of its quantity of at least one of the compounds of this invention. Color changes are very desirable for certain techniques, for example in the manufacture of printing plates, because they render it possible to examine the copying result even before development of the exposed plate. The acid donors disclosed in DE-A 23 31 377 and DE-A 26 41 100 are advantageously replaced by the compounds according to the present invention.

With particular advantage, the compounds according to this invention are used in mixtures which, in addition to the compounds of the invention, contain, as an essential component, a compound containing at least one acid-cleavable C-O-C grouping.

The following substances are examples of preferably used acid-cleavable compounds:

- A. Compounds containing at least one ortho-carboxylic acid ester grouping and/or carboxylic acid amide-acetal grouping, whereby the compounds may also have a polymeric character and the above-mentioned groupings may be present as connecting members in the main chain or as lateral substituents.
- B. Polymeric compounds with recurrent acetal and/or ketal groupings in which preferably both C-carbon atoms of the alcohols required for forming these groupings are aliphatic.

Acid-cleavable compounds of type A are described in detail as components of radiation sensitive compositions in DE-A 26 10 842 and DE-A 29 28 636, copying compositions containing compounds of type B are the subject of DE-C 27 18 254.

Acid-cleavable compounds also include, for example, the particular aryl-alkyl-acetals and -aminals disclosed in DE-C 23 06 248, which are also decomposed by the photolysis products of the compounds according to the present invention. Further compounds of this type are enolic ethers and acyl-iminocarbonates, as disclosed by EP-A 6,626 and 6,627.

Compositions in which molecules which essentially influence the chemical and/or physical properties of the composition by their presence, are directly or indirectly converted into smaller molecules by the action of actinic radiation, normally show an increased solubility, tackiness or volatility in the exposed areas. These areas can be removed by suitable procedures, for example by dissolving them away by means of a suitable developer liquid. In the case of copying materials, such systems are referred to as positive-working systems.

The novolak condensation resins which have proved suitable for many positive-working copying compositions have also been found to be suitable and advantageous additives in those cases where the compounds according to this invention are used in compositions containing acid-

cleavable compounds. These resins, in particular the more highly condensed resins containing substituted phenols as formaldehyde condensation partners, promote a strong differentiation between the exposed and the unexposed areas of the layer during development. The type and quantity of the novolak resins added may vary with the intended use of the composition; novolak proportions between 30 and 90 percent by weight, especially between 55 and 85 percent by weight, based on the total solids content of the composition, are preferred. In addition to or instead of novolaks, it is also advantageous to use other resins carrying phenolic groups. Additionally, co-use of numerous other resins is possible, vinyl polymers, such as polyvinyl acetates, polyacrylates, polyvinyl ethers, and polyvinylpyrrolidones, which, in turn, may be modified by co-monomers, being preferred. The most favorable proportion of these resins depends on practical technical requirements and on their influence on the conditions of development; normally it does not exceed 20 percent of the novolak component. For special requirements, such as flexibility, adhesion, gloss etc., minor amounts of other substances, such as polyglycols, cellulose derivatives, e.g. ethyl cellulose, surfactants, dyestuffs, finely divided pigments, and, if appropriate, UV absorbers may be added to the light-sensitive composition.

Preferably, development is performed with the aqueous-alkaline developers customary in the art, to which small proportions of organic solvents may be added. Organic solvents may be used for developing photopolymerizable mixtures.

The supports mentioned in connection with the photopolymerizable compositions may also be used for positive-working copying materials. In addition, the silicon, silicon nitride, silicon dioxide, metal and polymer surfaces known from microelectronic processes may be used.

The quantity of compounds of this invention, which are contained as photoinitiators in the positive-working mixtures, may vary widely, depending on the substance used and the type of the layer. Favorable results are obtained with proportions ranging from 0.05 percent to 12 percent, based on the total solids content, proportions between 0.1 and 8 percent being preferred. In the case of layers of more than 10 μm thickness, it is recommended to use a relatively small quantity of acid donor.

In principle, any electromagnetic radiation of a wave length up to about 550 nm is suitable for exposure. The preferred wave length range extends from 220 to 500 nm.

The great number of compounds according to this invention with absorption maxima well in the visible range of the spectrum and absorption ranges extending beyond 500 nm make it possible to select a photoinitiator which is optimally adapted to the light source employed. In principle, sensitization is also possible. On the other hand, it is also possible and advantageous in accordance with this invention to use the same photoinitiator in radiation-sensitive mixtures which are exposed to radiation emitted by different sources, i.e., to radiation of different wave lengths. A great number of

photoinitiators according to the invention show good results both in radiation-sensitive mixtures which are processed using automatic exposure apparatuses equipped with argon-ion lasers and in copying materials which are exposed by means of metal halide doped mercury high-pressure lamps. Further suitable light sources are, for example:

tubular lamps, pulsed xenon lamps and carbon arc lamps. In addition thereto, the light-sensitive mixtures according to the invention may be exposed in conventional projectors and enlargement apparatuses, to the light of metallic-filament lamps, and by contact exposure under normal incandescent bulbs. Alternatively, other laser beams may be used for exposure. Short-wave lasers of adequate energy output, for example excimer lasers, krypton-ion lasers, dyestuff lasers, and helium-cadmium lasers emitting in particular between 190 and 550 nm were found to be suitable for the purpose of this invention.

As a further possibility, differentiation may be performed by irradiation with electron beams. Like numerous other organic materials, mixtures containing one of the compounds according to this invention and a compound which can be split by an acid, can be thoroughly decomposed and cross-linked by electron beams, so that a negative image is formed after the unexposed areas have been removed by means of a solvent or by exposure without an original followed by development. In the case of an electron beam of lower intensity and/or higher writing speed, however, the electron beam causes a differentiation

toward a higher solubility, i.e. the irradiated areas of the layer may be removed by a developer. The most favorable conditions can be easily ascertained by preliminary tests.

Preferably, the radiation-sensitive mixtures containing one of the compounds according to the present invention are used for the manufacture of printing forms, especially offset printing forms, halftone gravure printing forms, and screen printing-forms, but also in photoresist solutions and in dry resists.

Radiation-sensitive mixtures containing one of the compounds according to this invention are advantageously also used for the manufacture of adhesive films according to WO-A 81/02261, instead of the naphthyl-bis-trichloromethyl-s-triazines mentioned in that publication.

A more detailed explanation of the invention will be given by the examples which follow. In the examples, parts by weight (p.b.w.) and parts by volume (p.b.v.) bear the same relationship as the g and the ml. Unless otherwise specified, percentage and volume data are to be understood as weight units.

Initially, the preparation of a number of the novel arylvinylphenyl-bis-trichloromethyl-s-triazines is described, which were tested in light-sensitive mixtures according to the invention as compounds which split off an acid and produce free radicals. These compounds were given the numbers 1 to 19 and will be referred to by

these numbers in the individual examples. Some of the arylvinylphenyl carbonitriles corresponding to formula III, which were employed as starting compounds, are known from literature, the others were prepared by analogy with the method described for their simplest representative.

For the preparation of nitriles serving as starting compounds for compounds Nos. 2 to 12, 18 and 19, too, 4-cyano-phenylmethanephosphonic acid diethyl ester, as the P-O-activated component, was reacted with the aldehyde Ar-CHO in accordance with the nomenclature employed in table I; to prepare the compound 16, the reaction is performed with acetophenone. In the preparation of the starting nitrile for compound 17, the P-O-activated component was 2-cyano-phenylmethanephosphonic acid diethyl ester. 2-Chloro-4-cyano-phenylmethanephosphonic acid diethyl ester was used to synthesize the starting nitriles of compounds 13 to 15. The phosphonic acid ester was obtained in the following way: Via the acid chloride and the amide, 3-chloro-4-methyl-benzoic acid was converted, by dehydration with thionyl chloride, into the 3-chloro-4-methyl-benzonitrile; the 3-chloro-4-methyl-benzonitrile was converted into the 4-bromomethyl-3-chloro-benzonitrile by reacting with N-bromo-succinimide dissolved in tetrachloro-methane, and from the 4-bromomethyl-3-chloro-benzonitrile the phosphonic acid ester was obtained by reacting it with triethyl phosphite.

General prescription for the preparation of arylvinyl-phenyl carbonitriles by means of the preparation of stilbene-4-carbonitrile

A solution of 0.1 mole of benzaldehyde in 0.105 mole of 4-cyano-phenylmethanephosphonic acid diethyl ester is dropwise added, in the course of 2 hours, to a vigorously stirred mixture of 22 g of pulverized potassium hydroxide and 200 ml of dimethyl formamide which is cooled with ice. Stirring is then continued for 1 hour with cooling and for another hour without cooling. Thereafter, the mixture is poured in 1 liter of ice water containing 52 ml of concentrated hydrochloric acid. The precipitate is removed by suction, freed from chloride ions by washing with water, dried and recrystallized from methanol.

Stilbene-4-carbonitrile having a melting point of 116-118°C is obtained in a quantity corresponding to 84 % of theoretical.

General prescription for the preparation of 2-(4-aryl-vinylphenyl)-4,6-bis-trichloromethyl-s-triazines by means of the preparation of 2-(4-styrylphenyl)-4,6-bis-trichloromethyl-s-triazine

At a temperature of 24 to 28°C, hydrogen chloride is added to a stirred suspension of 0.5 mole of stilbene-4-carbonitrile, 3 moles of trichloroacetonitrile and 0.06 mole of aluminum tribromide up to the point of saturation.

During this step, the solids dissolve almost completely. Then a precipitate is formed, the content of the flask gets a paste-like consistency, and splitting off of hydrogen chloride starts. For 6 hours, the mixture is kept at a temperature of 28-30°C by cooling, then it is allowed to rest for 24 to 48 hours at room temperature. The reaction mixture is dissolved in 1.6 liters of methylene chloride, the solution is neutralized by washing with water and dried over sodium sulfate. Then the solvent is distilled off under reduced pressure, the residue is dissolved in 600 ml of methylene chloride and 1,700 ml of methanol are added to the solution. 210 g (85 % of theoretical) of 2-(4-styrylphenyl)-4,6-bis-trichloromethyl-s-triazine still containing small amounts of impurities crystallize, which can be further purified by recrystallization from methylene chloride/methanol. Double melting point 160-163°C and 170-173°C.

AlCl_3 is also a suitable catalyst. Borotrifluoride etherate is a less effective catalyst, but it yields very pure reaction products.

The triazines listed in Table I are prepared according to the described procedure, whereby in some cases purification is performed chromatographically.

Table I Bis-trichloromethyl-s-triazines of the general formula I
with $R^2 = H$; $R^5 = H$;

Com- pound No.	Ar	R^1	R^3	$R^{4'}$	R^6	R^7	R^8	λ (EtOH)/log ϵ	Melting point (°C)
1	II	H	H	X	H	H	H	371 nm/4.62	160-163 and 170-173
2	"	H	H	X	H	H	4-CH ₃ O	395 nm/4.60	203-207
3	"	H	H	X	H	H	4-CH ₃	381 nm/4.61	188-192
4	"	H	H	X	H	H	4-Cl	371 nm/4.65	192-194
5	"	H	H	X	2-Cl	H	H	362 nm/4.62	208-210
6	"	H	H	X	H	3-Cl	H	365 nm/4.64	193-196
7	"	H	H	X	H	H	4-Br	371 nm/4.65	210-211
8	"	H	H	X	H	3-CH ₃ O	4-CH ₃ O	400 nm/4.57	126-129
9	"	H	H	X	H	3,4-OCH ₂ O		398 nm/4.57	180-184
10	"	H	H	X	H	H	4-C ₂ H ₅ O	397 nm/4.60	189-193

X = 4,6-bis-trichloromethyl-s-triazin-2-yl

Table I Bis-trichloromethyl-s-triazines of the general formula I
(Contd.) with $R^2 = H$; $R^5 = H$;

Com- pound No.	Ar	R ¹	R ³	R ⁴	R ⁶	R ⁷	R ⁸	λ (EtOH)/log ϵ	Melting Point (°C)
11	Formula I	H	H	X	5-CH ₃ O	3-CH ₃ O	4-CH ₃ O	389 nm/4.58	209-214
12	"	H	H	X	H	H	4-n-C ₆ H ₁₃	382 nm/4.51	75-77
13	"	H	Cl	X	H	H	H	369 nm/4.56	215-219
14	"	H	Cl	X	H	3-Cl	H	362 nm/4.58	191-194
15	"	H	Cl	X	H	H	4-CH ₃	379 nm/4.56	210-213
16	"	CH ₃	H	X	H	H	H	355 nm/4.35	169-172
17	"	H	X	H	H	H	H	372 nm/3.80	107-111
18	Naphth-1-yl	H	H	X				385 nm/4.51	210-214
19	Anthrac-9-yl	H	H	X				408 nm/4.20	160-172

X = 4,6-bis-trichloromethyl-s-triazin-2-yl

Example 1

Aluminum plates, the surfaces of which have been electrochemically roughened, anodically oxidized and pretreated with 0.1 % strength aqueous solutions of polyvinylphosphonic acid are coated with solutions of

6.63 p.b.w. of a cresol/formaldehyde novolak (melting range 105-120°C, according to DIN 53181)

1.99 p.b.w. of a polymeric orthoester, prepared by condensing orthoformic acid trimethyl ester with 4-oxa-6,6-bis-hydroxymethyl octan-1-ol

0.33 p.b.w. of compound No. 1 and

0.05 p.b.w. of crystal violet base, in

30 p.b.w. of ethylene glycol monomethyl ether,

52 p.b.w. of tetrahydrofuran and

9 p.b.w. of butyl acetate,

in a way such that a layer having a thickness of about 2.0 μm results after drying. The light-sensitive layer is exposed through an original which in addition to line and screen patterns contains a continuous tone step wedge with 13 steps which each have an optical density increment of 0.15, exposure being made with a 5 kW metal halide lamp for 15 seconds, at a distance of 110 cm. After a waiting time of 10 minutes, development is performed during 1 minute, using a developer of the following composition:

5.5 p.b.w. of sodium metasilicate x $9\text{H}_2\text{O}$,
3.4 p.b.w. of trisodium phosphate x $12\text{H}_2\text{O}$,
0.4 p.b.w. of sodium dihydrogen phosphate,
anhydrous, and
90.7 p.b.w. of water.

A positive image of the original is obtained. A printing test in an offset machine with the printing form prepared in this way is stopped after 140,000 prints, without any signs of impairment of the image quality being observed.

The copying result - measured by means of the number of developed continuous tone steps - which is achieved in this Example is also reached when compound No. 1 is replaced by the same quantity of one of compounds Nos. 3, 4, 5, 6, 7, 12 or 13 or of mixtures of these compounds, respectively.

If the particularly preferred initiators No. 5 and No. 20 of DE-C 27 18 259, 2-(4-ethoxynaphth-1-yl)- and 2-acenaphth-5-yl-4,6-bis-trichloromethyl-s-triazine are given the light-sensitivity factors 100 and 125, factors between 135 and 140 have to be attributed to the above-mentioned photoinitiators.

Example 2

Printing plates sized 580 mm x 420 mm and consisting of aluminum foil, the surface of which has been

electrochemically roughened, anodically oxidized and pretreated with polyvinylphosphonic acid and provided with a light-sensitive layer of the following composition:

73.96 p.b.w. of the novolak of Example 1,
22.19 p.b.w. of the polyorthoester of Example 1,
3.70 p.b.w. of photoinitiator and
0.15 p.b.w. of crystal violet base

are subjected to line-by-line exposure by means of the UV radiation of an argon ion laser in a (R) Laserite apparatus, whereby the number of written lines/cm is stepwise increased. The performance of the laser is kept constant during this procedure. The exposed printing plate is stored at room temperature for 10 minutes, then developed with the developer of Example 1 for 60 seconds and subsequently inked with greasy ink. When a certain number of lines/cm is exceeded the non-image areas are clear and no longer accept ink.

The minimum energy demand required for a scum-free developability of the non-image areas, which depends on the photoinitiator employed, can be calculated from the laser performance at the plate surface, the length of the lines, the number of lines/sec and the found number of lines/cm. These energy values are compiled in the following table:

<u>Compound</u>	<u>Minimum energy demand (mJ/cm²)</u>
1	6.5
3	7.5
4	6.7
5	5.6
6	6.5
7	6.5
12	7.8
13	5.6
14	7.2
16	7.3

For comparison:

2-(4-ethoxynaphth-1-yl)- 4,6-bis-trichloromethyl- s-triazine	8.4
2-acenaphth-5-yl- 4,6-bis-trichloromethyl- s-triazine	11.2
2-(4-methoxystyryl)- 4,6-bis-trichloromethyl- s-triazine	9.2

The comparison shows that the photoinitiator 2-acenaphth-5-yl-4,6-trichloromethyl-s-triazine, which is highly active when being exposed to the emission of metal

halide lamps, but nevertheless is exceeded by the novel photoinitiators in this field of application, has a minimum energy demand in the case of laser irradiation which is 100 % higher than that of compounds No. 5 and No. 13.

Example 3

A layer of the following composition, coated onto a mechanically roughened aluminum foil from a 10 % solution in methyl ethyl ketone, is exposed for 5 seconds under the same conditions as in Example 1 and developed for 45 seconds with the developer of Example 1:

76.63 p.b.w. of phenol/formaldehyde novolak (melting range 110-120 °C, according to DIN 53181),
19.16 p.b.w. of the polyacetal of 2-ethylbutyraldehyde and triethylene glycol,
3.83 p.b.w. of compound No. 18, and
0.38 p.b.w. of crystal violet base.

A printing form carrying a positive image of the original is obtained.

The sensitivity achieved with compound No. 19 is slightly reduced.

Example 4

The suitability of the novel bis-trichloromethyl-s-triazines as initiators in compositions which are sensitive to electron beams is demonstrated below:

Layers composed of

- 73 p.b.w. of the novolak of Example 1,
- 22 p.b.w. of the bis-(5-butyl-5-ethyl-1,3-dioxan-2-yl) ether of 2-butyl-2-ethyl-propane diol, and
- 5 p.b.w. of one of compounds No. 2, No. 9 and No. 10

are applied, in a thickness of about 1.1 μm , to mechanically roughened aluminum and irradiated with 11 kV electrons.

At a beam current of 5 μA , an irradiation time of 4 seconds is sufficient to render an area of 10 cm^2 soluble after developing for 60 seconds with the developer of Example 1; this corresponds to a sensitivity of the above-mentioned layers of 2 $\mu\text{C}/\text{cm}^2$.

Example 5

A plate of electrolytically roughened and anodically oxidized aluminum is spin-coated with a coating solution composed of

- 6.7 p.b.w. of trimethylolethane triacrylate
- 6.5 p.b.w. of a copolymer of methyl methacrylate and methacrylic acid, acid number 115,
- 0.12 p.b.w. of compound No. 1
- 64.0 p.b.w. of ethylene glycol monoethyl ether
- 22.7 p.b.w. of butyl acetate and
- 0.3 p.b.w. of 2,4-dinitro-6-chloro-2'-acetamido-5'-methoxy-4'-(N- -hydroxyethyl-N- '-cyano-ethylamino)-azobenzene,

in a way such that a layer weight of 3 to 4 g/m² results after drying. Subsequently, the plate is provided with a 4 m thick protective layer of polyvinyl alcohol (K-value 4; 12 % of residual acetyl groups), exposed under a line and screen original by means of a 5 kW metal halide lamp, for 22 seconds at a distance of 110 cm, and developed with a 1.5 % strength solution of sodium metasilicate.

A negative image of the original is obtained. A print test with an offset printing plate prepared in this way was stopped after 200,000 prints, without any impairment of the quality being observed.

Example 6

The example describes a negative dry resist. The following coating solution, of

- 24.9 p.b.w. of a copolymer of 30 p.b.w. of methacrylic acid, 60 p.b.w. of n-hexyl-methacrylate and 10 p.b.w. of styrene,

16.1 p.b.w. of the reaction product of 1 mole of
2,2,4-trimethylhexamethylene diisocyanate
and 2 moles of hydroxyethyl methacrylate,
0.41 p.b.w. of triethylene glycol dimethacrylate,
0.58 p.b.w. of compound No. 5,
0.11 p.b.w. of the dyestuff used in Example 5, and
57.9 p.b.w. of methylethyl ketone

is spin-coated on a polyethylene terephthalate film, in a way such that a dry layer weight of $\sim 25 \text{ g/m}^2$ is obtained. The resulting material is laminated, in a commercially available laminator, at 120°C , onto a support of insulating material which is provided with a $35 \mu\text{m}$ thick copper layer. After exposing the material for 60 seconds through an original which in addition to line and screen patterns includes a continuous tone step wedge, by means of the light source of Example 1, and development with an 0.8 % strength sodium carbonate solution, a negative image of the line and screen pattern and steps 1 to 6 of the continuous tone step wedge remain in the form of a raised relief, step 7 is partially corroded.

The resist layer obtained is resistant to etching processes, for example, with ferric chloride, and to the influences of electroplating baths used for the production of printed circuit boards.

Example 7

A plate of mechanically roughened aluminum is spin-coated with a solution of

4.3 p.b.w. of a phenol/formaldehyde novolak (melting range $110\text{-}120^\circ\text{C}$, according to DIN 53181),

10.6 p.b.w. of N-vinyl carbazole,
0.24 p.b.w. of 2-(p-dimethyl-amino-styryl)-benz-
thiazole,
0.25 p.b.w. of one of compounds No. 15 and No. 18,
and
84.6 p.b.w. of methyl ethyl ketone.

After drying, a light-sensitive layer having a thickness of about 1 to 2 μm is obtained. The plate is imagewise exposed for 7.5 seconds as described in Example 1, whereby the color of the layer changes from yellow to orange-red in the image areas. By moving the plate to and fro in a developer solution of

0.6 p.b.w. of NaOH,
0.5 p.b.w. of $\text{Na}_2\text{SiO}_3 \times 5 \text{H}_2\text{O}$,
1.0 p.b.w. of n-butanol and
97.9 p.b.w. of deionized water,

the unexposed layer portions are removed within 75 seconds. The exposed areas accept ink when the plate is wiped over with greasy ink, so that the plate prepared in this way can be used for printing on an offset machine. In the case of somewhat extended exposure times, it is also possible to use compounds No. 8, No. 11 and No. 17 instead of compounds No. 15 and No. 18.

Example 8

Example 7 is repeated with the exception that in the coating solution the styryl dye base is replaced by the

same amount of the cyanine dye base 2-(1-cyano-3-(3-ethyl-benzthiazolylidene-(2))-propen-1-yl) quinoline, that the compound No. 15 or No. 18 is replaced by the same amount of compound No. 3 and that a polyester film is coated.

When the plate is imagewise exposed for 12 seconds as in Example 1, the color of the image area changes from the initial light red to deep violet.

The non-image areas are removed by wiping the plate with the developer of Example 3. A negative image of the original is obtained.

This method can be employed for the production of color films.

Example 9

A mechanically roughened aluminum plate is spin-coated with a layer of the following composition, from a 10 % methyl ethyl ketone solution:

- 48.3 p.b.w. of an epoxy resin (of epichlorohydrin and bisphenol A, epoxy equivalent weight 182-194),
- 48.3 p.b.w. of the novolak of Example 1,
- 2.9 p.b.w. of compound No. 4, and
- 0.5 p.b.w. of crystal violet.

A negative image of the original, in which the non-image areas are free of scum, is produced by imagewise exposing the plate for 45 seconds as described in Example 1 and then developing it for 40 seconds with the developer of Example 7.

If the epoxy resin is replaced by the same amount of the above stated novolak, a negative image becomes briefly visible during development, but the resistance of the layer to the developer is so poor that the entire layer is dissolved from the support within 30 seconds.

Example 10

Thick layers of a positive working photoresist are prepared in the following way:

A solution of
60 p.b.w. of butanone,
30 p.b.w. of the novolak according to Example 1,
8.58 p.b.w. of a polyacetal of 2-ethyl hexanal and
pentane-1,5-diol,
0.12 p.b.w. of compound No. 7, and
1.3 p.b.w. of polyvinyl methyl ether

is applied, by means of a wire bar No. 40, to the cleaned copper surface of the laminate material of Example 6. The plate is stored for 12 hours at room temperature, so that most of the solvent evaporates, then it is post-dried for 15 minutes at 70°C by means of infrared radiation.

The 70 m thick resist layer obtained is exposed for 60 seconds through a line original by means of the light source used in Example 1 and can be developed within 40 seconds by spray development with an 0.8 % strength aqueous sodium hydroxide solution.

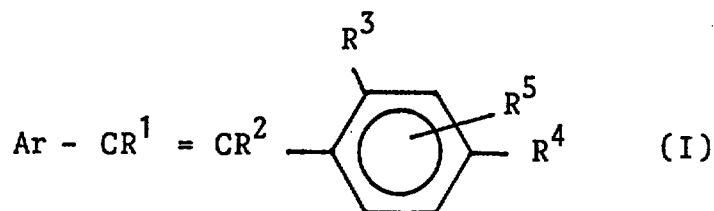
Example 11

A solution of
23.3 p.b.w. of the novolak according to Example 1,
6.9 p.b.w. of the bis-orthoester according to
Example 4, and
1.0 p.b.w. of compound No. 1, in
6.9 p.b.w. of xylene,
6.9 p.b.w. of butyl acetate and
55.0 p.b.w. of 2-ethoxy-ethyl acetate

is spin-coated, at 4,000 rpm, onto a silicon wafer which carries a 1.0 μm thick oxide layer and has a diameter of 7.6 cm. After 30 minutes' drying at 90°C in a circulating air drying cabinet, the resist layer has a thickness of 1.15 μm . The coated silicon disk is exposed through a mask in a contact exposure apparatus, using a mercury high pressure lamp. 5.6 mJ/cm^2 are sufficient to dissolve away the exposed areas of the resist layer within 90 seconds, by means of the developer of Example 1.

Claims:

1. Light-sensitive compounds of the general formula I



in which

R^1 and R^2 denote hydrogen atoms or methyl groups,

R^3 and R^4 are different from one another and each denote a hydrogen atom or a 4,6-bis-trichloromethyl-s-triazin-2-yl group,

R^5 denotes a hydrogen or halogen atom or an alkyl or alkoxy group, and

Ar is a phenyl group which may carry 1 to 3 substituents selected from the group including halogen atoms, alkyl, halogeno-alkyl, aralkyl, aryl-oxyalkyl, cycloalkyl, alkenyl, aryl or aryloxy groups, whereby in the alkyl groups individual methylene groups can be replaced by oxygen or sulphur atoms and two of these groups can each be linked to form a 5- or 6-member ring, and the maximum total number of carbon atoms contained in the substituents is 12;



or is a naphthyl, acenaphthyl, di- or tetrahydronaphthyl, indanyl, anthryl, phenanthryl, fluorenyl or tetrahydrophenanthryl group which can be substituted by halogen atoms, by alkyl groups having 1 to 3 carbon atoms, by alkoxy groups having 1 to 4 carbon atoms or by alkoxy-alkyl groups having 3 to 6 carbon atoms.

2. Compounds as claimed in Claim 1, wherein R^1 , R^2 , R^3 , and R^5 are hydrogen atoms.

3. Light-sensitive mixture containing a bis-trichloromethyl-s-triazine (a) and a compound (b) which is capable of reacting with the photoreaction product of the triazine (a) in such a way that a product is formed, the light absorption or solubility in developer of which is different from that of (b), characterized in that the triazine (a) is a compound of the general formula I as claimed in Claim 1.

4. Light-sensitive mixture as claimed in Claim 3, wherein the compound (b) is an ethylenically unsaturated compound which is capable of undergoing a polymerization reaction initiated by free radicals.

5. Light-sensitive mixture as claimed in Claim 3, wherein the compound (b) contains at least one acid-cleavable C-O-C-bond.



6. Light-sensitive mixture as claimed in Claim 3, wherein the compound (b) can be induced by an acid to undergo a cationic polymerization.

7. Light-sensitive mixture as claimed in Claim 3, wherein the compound (b) can be cross-linked by an acid.

8. Light-sensitive mixture as claimed in Claim 3, wherein the color of the compound (b) changes by the action of an acid.

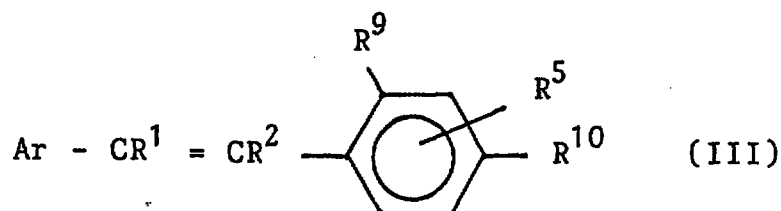
9. Light-sensitive mixture as claimed in Claim 3, wherein the compound of the general formula I is contained in an amount of between 0.05 and 10 % by weight, relative to its non-volatile constituents.

10. Light-sensitive mixture as claimed in Claim 3, wherein additionally a water-insoluble polymeric binder is contained.

11. Light-sensitive mixture as claimed in Claim 10, wherein the binder is soluble in aqueous-alkaline solutions.

12. Process for the production of a compound of the general formula I as claimed in Claim 1, wherein 1 mole of a compound of the general formula III





in which

R^9 and R^{10} are different from one another and each denote a hydrogen atom or a CN-group, and Ar , R^1 , R^2 have the same meaning as in Claim 1, and R^5

and 2 to 8 moles of trichloroacetonitrile are cotri-
merized in the presence of hydrogen halide and Friedel-
Crafts catalysts.

