Patented Dec. 22, 1953

2,663,640

UNITED STATES PATENT OFFICE

2,663,640

PHOTOGRAPHICALLY LIGHT-SENSITIVE SILVER HALIDE - DIAZIDE COLLOID LAYERS

Maximilian Karl Reichel and Wilhelm Neugebauer, Wiesbaden-Biebrich, Germany, assignors to Keuffel & Esser Comp., Hoboken, N. J.

No Drawing. Application October 13, 1950, Serial No. 190,042

Claims priority, application Germany October 24, 1949

8 Claims. (Cl. 95—7)

1

The present invention relates to a type of photosensitive material commonly used as an intermediate reproduction material in the drafting art. This photosensitive material is commonly used to make duplicate tracings from which prints can be made by the ordinary reproduction methods. The particular type of material to which the invention relates is made by coating on a suitable base a colloid layer (such as glue) containing a silver halide and an agent capable of hardening or tanning the colloid under the influence of light. The base for this type of photosensitive material is ordinarily tracing cloth which has been waterproofed by means of a nitrocellulose lacquer. However, tracing paper and other suitable materials may also be used as a base.

Photosensitive materials of the type described are exposed to light under a negative original (usually a brown-print made from a tracing) and washed with water to remove the colloid layer from the unexposed areas. They are then developed with a photographic developing solution to form a black silver relief image of the exposed areas.

Chromates have been used as the hardening agent for the colloid in the photosensitive material of this type known in the art. However, the stability of the materials containing chromates has long been recognized as not being as good as desirable. It was therefore necessary to take special care in storing such materials and even then they could not be prepared too long a time before use.

Chromates are also generally used in other photosensitive layers; e. g. those used in lithography. These layers contain colloids such as glue but do not contain silver halides. Many attempts have been made to replace the poisonous chrome salts in this latter type of photosensitive layers with other substances which would have the same hardening action on colloids upon exposure to light. Particularly light-sensitive diazo compounds whose light decomposition products are able to tan colloids (U. S. Patent No. 2,100,063), nitro-derivatives of polyhydroxy compounds (U. S. Patent No. 2,090,450) and aromatic aldehydes, such as anis aldehyde have been proposed as substitutes for chromates. More recently aromatic azides have also been proposed. Among the best azides which have been recommended for tanning colloids upon exposure to light are the azidostyrylketones and azidostyrylaryl azides.

Light sensitive colloid layers containing azido

2

compounds (as compared to those containing chromates) are characterized by a highly improved shelflife. Nevertheless, satisfactory results were not obtained when azido compounds were first used in colloid layers containing silver halides. The reason for this is probably that the presence of inorganic salts in colloidal layers inhibits to a large extent the performance of the tanning or hardening of the colloidal substance and that the tanning action may even be compensated completely by high concentrations of said compounds. For these reasons, photosensitive colloid layers containing silver halides in which azido compounds are used in place of chromates have not been introduced into practice.

The principal object of the present invention is to increase the shelf life of light sensitive photographic layers containing colloid substances and silver halides by substituting aromatic azido compounds for the di-chromates conventionally used as hardening agents for the colloid.

The azido compounds which have been found to be useful in colloid layers containing silver halides are diazidostilbene compounds in which the azido groups are symmetrically arranged. The ratio of the weight of the diazido-stilbene to the dry weight of the colloidal substance should not be less than 1:4. The optimum ratio has been found to be about 1:3.

It is also important that there should not be a large excess of alkali metal halide present in the colloid layer. An alkali metal halide is usually used in combination with silver nitrate in order to form the silver halide in the colloid. The simplest way in which to make sure that there will not be a large excess of alkali metal halide is to add the alkali metal halide and silver nitrate to the colloidal dispersion in substantially stoichiometric proportions or with only a slight excess of alkali metal halide.

For the purpose of the present invention the diazido-stilbene compounds used must be soluble in water. Hence it follows that diazido-stilbenes are suitable which can easily be transformed into water soluble compounds, for example, into salts. Diazido-stilbenes of this kind are diazido-stilbene-sulfonic acids and diazido-stilbene-carboxylic acids both with two symmetrically arranged azido groups in the molecules, such for example, as 4,4'-diazido-stilbene-2,2'-disulfonic acid and 4,4'-diazido-stilbene-2,2'-dicarboxylic acid. These acids are used preferably in the form of their alkali metal salts.

The base-material used to support the new

colloid layers made according to the present invention may be identical with the base-material ordinarily used in the art (i. e. waterproofed tracing cloth). However, foils of cellulose acetate, metallic plates, metallic foils particularly those which may be subjected to a surface-treatment, such as surface oxidation, surface-roughening and so on may also be used to carry these photosensitive layers. The colloidal substances which may be used in the new process are also the same as those known in the art: i. e., fish glue, gelatine, polyvinyl-pyrrolidone, polyvinyl alcohol and so on. They may be used separately or in combination with each other.

The new light-sensitive layers, produced in accordance with the present invention containing sufficient quantities of diazidostilbene compounds in place of chromates as the tanning agent, are far superior to the hitherto known colloid layers containing silver halide and chromate of like tanning capacity and light-sensitivity, especially with regard to their shelf-life in the light sensitive state and they are at least equal to the known products with regard to tanning power and sensitivity to light.

These photosensitive layers free from chromate offer a further advantage insofar as it is possible to use also more transparent supports than tracing cloth, such as superficially saponified acetyl cellulose which is less suitable for chromate silver halide colloid layers under like working conditions.

Photosensitive material coated with colloid layers containing chromate and silver salt, when stored for a long period of time, even under the most favorable conditions, forms, after exposure to light and development with a soda alkaline metol-hydroquinone solution, black layers of finely distributed silver spread over the whole surface of the image. Said black silver layers are very difficult to remove without damaging the image. The chromate-free photographic colloid layers in which in accordance with this invention diazidostilbene compounds are used as tanning agent have not the above described disadvantage. They develop clear and need only a treatment with running tap water in order to remove the developer solution prior to the drying of the copy.

The following examples are inserted to illustrate the invention.

1. To an emulsion consisting of

5 liquid ounces of Le Pages photographic glue, and
77 liquid ounces of distilled water

are slowly added dropwise while under constant stirring out of two burettes

a. 9 liquid ounces of silver nitrate solution (3.07 ounces by weight of dry salt in distilled water)

and

b. 9 liquid ounces of potassium chloride solution (1.43 ounces by weight of potassium chloride dissolved in distilled water).

To this milk-like emulsion 2 ounces by weight of 4,4'-diazidostilbene 2,2'-disulfonic acid sodium salt dissolved in 10 liquid ounces of distilled water, are slowly added dropwise, while stirring constantly. The emulsion mixture is applied to a base. Suitable bases are, for example, tracing cloth coated with a nitrocellulose lacquer, superficially saponified acetylcellulose foils and others. After exposure to light under a negative pattern, the colloid areas not exposed to light may be removed with running tap water. The silver image is then developed with an aqueous soda alkaline metol-hydroquinone solution consisting of

4 grams of metol,
12 grams of hydroquinone,
12 grams of sodium carbonate (free from water),
44 grams of sodium sulfite (crystallized)

in sufficient distilled water to make a total volume of 2250 cc. A black silver image on a clear background is obtained. The black silver image is distinguished by an excellent absorption power for short wave length light.

This light-sensitive material free from chromates has unlimited stability and is distinctly different from the hitherto known colloid layers containing silver halide and chromate.

2. The same photosensitive glue-gelatin colloid layer containing silver salt is used as described in Example 1, but in lieu of 2 ounces of 4,4'-diazidostilbene-2,2'-disulfonic acid sodium salt, 2 ounces of 4,4'-diazidostilbene-2,2'-dicarboxylic acid sodium salt are added.

3. The same photosensitive colloid described in Example 1 is coated on a saponified cellulose acetate foil having a saponified surface and after drying it is exposed to light under a negative pattern. Thereafter those areas of the colloid layer not exposed to light are washed off with running tap water, and developed with the aid of the aqueous soda alkaline metol-hydroquinone solution. A black silver image on a clear white background is obtained.

After having fully described and explained our present invention, what we claim is:

1. As a new article of manufacture light-sensitive material comprising a suitable base material and a light-sensitive colloid layer substantially free of alkali metal halides on said base material said light-sensitive colloid layer comprising a light hardenable solloid, silver halide and a water-soluble salt of a diazido compound selected from the group consisting of diazidostilbene-sulfonic acids and diazido-stilbene carboxylic acids with symmetrically arranged azido groups, the ratio of the weight of said salt of said diazido compound to the dry weight of said light hardenable colloid being not less than 1:4.

2. As a new article of manufacture light-sensitive material comprising a suitable base material and a light-sensitive colloid layer substantially free of alkai metal halides on said base material, said light-sensitive colloid layer comprising a light hardenable colloid, silver halide and an alkali salt of 4,4'-diazido-stilbene-2,2'-disulfonic acid, the ratio of the weight of said diazidostilbenedisulfonic acid sodium salt to the dry weight of said light hardenable colloid being not less than 1:4.

3. As a new article of manufacture light sensitive material comprising a suitable base-material and a light-sensitive colloid layer substantially free of metal halides on said base material, said light-sensitive colloid layer comprising a light hardenable colloid, silver halide and an alkali salt of 4,4'-diazidostilbene-2,2'-dicarboxylic acid, the ratio of the weight of said diazidostilbenedicarboxylic acid alkali salt to the dry weight of said light hardenable colloid being not less than 1:4.

4. As a new article of manufacture light-sensitive material comprising a waterproofed tracing cloth base material and a light-sensitive colloid layer substantially free of alkali metal halides on said base material, said light-sensitive colloid

layer comprising a light hardenable colloid, silver halide and a water soluble salt of a diazido compound selected from the group consisting of diazido-stilbene-sulfonic acids and diazido-stilbene carboxylic acids with symmetrically arranged azido groups, the ratio of the weight of said salt of said diazido compound to the dry weight of said light hardenable colloid being not less than 1:4.

5. As a new article of manufacture light-sensitive material comprising a cellulose acetate foil having a saponified surface as a base material and a light-sensitive colloid layer substantially free of alkali metal halides on said saponified surface of said cellulose acetate foil base material, said light-sensitive colloid layer comprising a light hardenable colloid, silver halide and a water soluble salt of a diazido compound selected from the group consisting of diazido-stilbene-sulfonic acids and diazido-stilbene carboxylic acids with symmetrically arranged azido groups, the ratio of the weight of said salt of said diazido compound to the dry weight of said light hardenable colloid being not less than 1:4.

6. The process for the production of light-sensitive material capable of producing a black silver relief image comprising the steps of adding substantially stoichiometric quantities of alkali metal halide and a soluble silver salt to an aqueous dispersion of a light hardenable colloid, adding in the form of a water soluble salt a diazido compound selected from the group consisting of diazido-stilbene-sulfonic acids and diazido-stilbene-carboxylic acids with symmetrically arranged azido groups to said colloid dispersion, the ratio of the weight of the diazido-stilbene compound to the dry weight of the light hardenable colloid being not less than 1:4 and coating said aqueous dispersion on a base material to form a photosensitive colloid layer thereon.

7. The process for the production of light-sensitive material capable of producing a black silver relief image comprising the steps of adding substantially stoichiometric quantities of alkali metal halide and a soluble silver salt to an aqueous dispersion of a light hardenable colloid, adding an alkali salt of 4,4'-diazido-stilbene-2,2'-disulfonic acid to said colloid dispersion, the ratio of the weight of the diazido-stilbene compound to the dry weight of the light hardenable colloid being not less than 1:4 and coating said aqueous dispersion on a base material to form a photosensitive colloid layer thereon.

8. The process for the production of light-sensitive material capable of producing a black silver relief image comprising the steps of adding substantially stoichiometric quantities of alkali metal halide and a soluble silver salt to an aqueous dispersion of a light hardenable colloid, adding an alkali salt of 4,4'-diazido-stilbene-2,2'-dicarboxyic acid to said colloid dispersion, the ratio of the weight of the diazido-stilbene compound to the dry weight of the light hardenable colloid being not less than 1:4 and coating said aqueous dispersion on a base material to form a photosensitive colloid layer thereon.

MAXIMILIAN KARL REICHEL.
WILHELM NEUGEBAUER.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,564,161	Weingarten	Dec. 1, 1925
1,984,090	Seymour	Dec. 11, 1934

FOREIGN PATENTS

Number	Country	Date
886,716	France	July 12, 1943
232,145	Switzerland	Aug. 1, 1944