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2,942,975

PHOTOSENSITIVE MATERIAL

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This invention relates to a type of photosensitive material commonly used as an intermediate reproduction material in the drafting art. It can be used to make duplicate tracings from which additional prints can be made by the ordinary reproduction methods. The particular type of material to which the invention relates is made by coating a suitable light transmitting base such as tracing cloth, tracing paper and other transparentized bases or naturally transparent or translucent bases with a colloid layer containing a silver halide and an agent capable of hardening a colloid under the influence of light. The base for this type of photosensitive material may for example be tracing cloth which has been coated with a lacquer to make it waterproof, then coated with a subbing layer and finally coated with the light sensitive layer described above. The purpose of the subbing layer is to promote adhesion between the light sensitive layer and the waterproofed base material. The substratum also affects some characteristics of the sensitive layer, such as printing speed, gradation (contrast), keeping quality, etc.

Photosensitive materials of the type described are exposed to light under a negative original which may be a brownprint made from a tracing or a drawing on transparent paper. After exposure, the material is washed with water to remove the colloid layer from the unexposed areas and then developed with a photographic developing solution to form a metallic silver relief image of the exposed areas which usually appears black.

For the most part, chromates have been used as the light sensitive hardening agent for the colloid in the photosensitive material of this type known in the art. However, Patent No. 2,663,640, which issued to M. K. Reichel and W. Neugebauer on December 22, 1953, discloses the use of diazido compounds as the light hardening agent in this type of material.

The subbing layer used in this type of material includes a protein colloid such as glue, gelatin and the like. It has been a practice to add a small amount of formaldehyde to increase the water resistance of the colloid and thereby improve the adhesion of the photosensitive layer to the base during the processing of the material to form the image thereon. Despite the use of this formaldehyde, one of the most effective colloid hardening agents known, it has been found that the adhesion of the photosensitive layer varies considerably from batch to batch in production which has been a great handicap in the commercial use of this type of reproduction material. In addition, the formaldehyde is objectionable because of its unpleasant odor.

Now it has been found that improved results are obtained by eliminating formaldehyde from the subbing and using a small amount of zirconium salt. The zirconium salt may either be used in a solution which is applied to the subbing layer or the zirconium salt may be incorporated with the protein colloid and coated on the base material therewith to form the subbing layer.

The principal objects of the present invention are to

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improve intermediate reproduction materials having a light sensitive layer including a colloid, a silver halide and a light-hardening agent by using a zirconium salt carried by the subbing for such layers and eliminating the objectionable effects resulting from the use of formaldehyde in such materials.

The principal zirconium salt which has found use according to the present invention is zirconium acetate having the approximate formula $H_2ZrO_2(C_2H_3O_2)_2$. However, other zirconium salt may be used such as zirconium oxychloride $Zr_2O_3Cl_2 \cdot 6H_2O$ ammonium zirconyl carbonate, $(NH_4)_3ZrOH(CO_3)_3 \cdot 2H_2O$ and zirconium sulphate, $Zr(SO_4)_2 \cdot 4H_2O$. When some of these salts are used, it may be necessary to adjust the pH. The best results are obtained if the pH of the wash solution containing the zirconium salt is adjusted to fall within a range close to the isoelectric point of the colloid used. In the case of a particular gelatin suitable for use in subbing layers, the pH of the wash solution used therewith should be between 4 and 6. It is also necessary to balance the ratio between the water and organic solvent used in the wash solution since if the percentage of organic solvents is too great, the zirconium salt may tend to separate out in the form of a gel.

The protein colloids which are useful in the subbing of the present invention are gelatin, glue, albumin, casein and zein.

The waterproofed layer which is applied to protect the tracing cloth may be a nitrocellulose lacquer or other types of lacquers may be used. A wide variety of resins may be incorporated in the waterproofed layer or multiple resin coats may be used such as vinyl resin coating followed by nitrocellulose both of which together may be considered to be the waterproofed layer. It is also customary to apply waterproofed layers to the back side of the material. Additional layers may also be applied to the back side in order to make the properties of this side similar to those of the photosensitive side of the material in order to prevent curling.

The practice of the invention is illustrated by the following examples:

Example I

A waterproofed tracing cloth was coated with a subbing layer of the following formula:

120 grams gelatin
8800 cc. methyl alcohol
1000 cc. glacial acetic acid
100 cc. water

Ethyl alcohol and/or acetone may replace all or part of the methyl alcohol in the above formula. Before coating the photosensitive layer on this subbing it was treated with a wash solution made up according to the following formula:

20 cc. zirconium acetate solution (this solution contains the equivalent of 14% ZrO_2)
350 cc. water
600 cc. organic solvents selected from methyl alcohol, ethyl alcohol, acetone and methyl ethyl ketone

Small percentages of wetting agents and flow agents may also be incorporated in this formula.

The material was then coated with a light sensitive coating made up according to the following formula:

To an emulsion consisting of:

5 liquid oz. of Le Page's photographic glue, and
77 liquid oz. of distilled water

are slowly added drop-wise while under constant stirring out of 2 burettes;

9 liquid oz. of silver nitrate solution containing 3.07 oz. by weight of dry salt in distilled water, and

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9 liquid oz. of potassium chloride solution containing 1.43 oz. by weight of potassium chloride in distilled water

To this milk-like emulsion are slowly added drop-wise while stirring constantly: .4 oz. by weight of potassium bichromate dissolved in 10 liquid oz. of distilled water.

Reproductions made on this photosensitive material exhibit sharp black lines against a clean background and the lines exhibit exceptional adhesion to the base. The excellent adhesion to the base material is maintained after accelerated aging tests.

Example II

A tracing cloth provided with a waterproofed lacquered coating was coated with a subbing layer made according to the following formula:

120 grams gelatin
9500 cc. methyl alcohol
1500 cc. glacial acetic acid
150 cc. water
120 cc. zirconium acetate solution containing the equivalent of 14% ZrO_2

Ethyl alcohol, acetone and methyl ethyl ketone may be used to replace all or part of the methyl alcohol in the above formula. Small quantities of wetting agents or flow agents may also be added to this subbing solution.

The base material provided with this subbing was coated with the same photosensitive material described in Example I and reproductions made with the material showed the same excellent properties and in particular, the same outstanding adhesion of the image areas to the base.

Example III

The waterproofed tracing cloth material subbed in accord with Example II was coated with a light sensitive composition exactly the same as that disclosed in Example I except that 2 oz. by weight of 4,4'-diazido-stilbene, 2,2'-disulfonic acid sodium salt dissolved in 10 liquid ounces of distilled water were substituted for potassium bichromate solution used in Example I.

Reproductions made with this material exhibited greater adhesion of the image areas to the base than diazide sensitized materials applied over a standard subbing.

Having thus described the invention what is claimed is:

1. A photosensitive material for producing a dark

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relief image comprising a base, a subbing layer including gelatin and a zirconium salt on said base, a light sensitive emulsion layer including a silver halide, photographic glue, and a light hardening agent selected from the group of dichromates and diazido compounds, said light sensitive layer being coated on said subbing layer whereby when the light sensitive layer is exposed to light the exposed portions of said light sensitive layer adhere securely to the subbing layer.

2. The invention according to claim 1 in which the base is of light transmitting material.

3. The invention according to claim 2 in which a waterproofing layer is provided on the base.

4. The invention according to claim 3 in which the waterproofing layer is nitrocellulose, the base is tracing cloth, the zirconium salt is zirconium acetate, and the hardening agent is a bichromate.

5. The invention according to claim 1 in which the hardening agent is a bichromate.

6. The invention according to claim 1 in which the hardening agent is a salt of 4,4'-diazido-stilbene, 2,2'-disulfonic acid.

7. The invention according to claim 1 in which the subbing layer has a pH of 4 to 7.

8. The invention according to claim 1 in which the pH of the subbing layer falls close to the isoelectric point of the gelatin.

9. The invention according to claim 1 in which the zirconium salt is applied by a wash to the subbing layer.

10. The invention according to claim 1 in which the zirconium salt is incorporated in the subbing layer prior to coating on the base.

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