

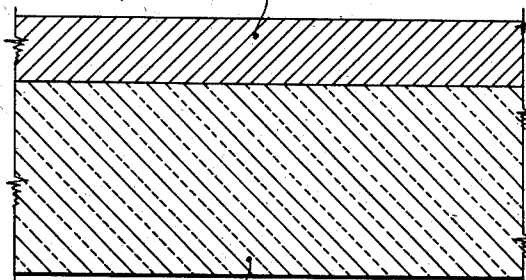
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PHOTOGRAPHICALLY SENSITIVE ELEMENT

1,962,307

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*Photosensitive layer containing heavy
metal sulfide and trivalent cobalt salt.*



Support.

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UNITED STATES PATENT OFFICE

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PHOTOGRAPHICALLY SENSITIVE ELEMENT

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5 Claims. (Cl. 95—7)

This invention relates to a positive photographic printing process of a novel type.

A positive printing process in which a black material would be bleached as a result of exposure to light has long been desired. We have now found a means of producing such a material of a useful sort.

We have discovered that certain heavy metal sulphides which are brown or black, may be oxidized to a white material, probably the corresponding sulphate, under the action of light, by certain salts. These salts are trivalent cobalt salts and through a photochemical reaction induced by light they oxidize the metal sulphide. Among the salts which we have found accomplish the oxidation are hexammine cobaltic-chloride $[\text{Co}(\text{NH}_3)_6\text{Cl}_3]$, nitrosopentamine cobaltic chloride $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$, and trinitro-triamine cobalt $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]\text{Cl}$.

The metal sulphides which are particularly useful are those of lead, copper, bismuth, nickel, mercury and silver. All of these are of a dark color. The cobalt salts are added to, or coated over, layers containing these sulphides as indicated.

The reaction in these cases is photochemical, that is, under the action of light the cobalt salt reacts to oxidize the metal sulphide. It is thus seen that it is possible to produce a dark colored coating of the metal sulphide containing one of these cobalt salts and by exposure to light to obtain a white design against a black background, the white portions corresponding to the areas of greatest light action. This we have made the basis of a practical printing method.

The following is illustrative of one method of carrying out our invention.

A suspension of lead sulphide in gelatin is made as follows:

Solution A

Lead acetate ----- 10 grams
Gelatin ----- 20 grams
Water ----- 100 cc.

After the solution of the gelatine and the lead acetate there is added to this solution the following:

Solution B

Sodium sulphide ----- 10 grams
Gelatin ----- 20 grams
Water ----- 100 cc.

After Solution B has been added to Solution A, as indicated, the entire solution is allowed to

set. It is then shredded, washed and remelted, in the manner well-known to photographic emulsion makers.

The mixture is now coated on a support such as paper, for example, in the usual manner, the coating being in a thin layer. After the coating is dried there is applied to its surface the following:

Solution C

Hexammine cobaltic chloride saturated solution (at room temperature) ----- 65
Citric acid ----- 5 grams per liter of above
Glycerin ----- 3 grams per liter.

When this second coating is dried, the paper is now ready to print. It is exposed to a light image, as for example, under a negative to a bright light, until the image is visible. At the points where the light has acted the dark colored lead sulphide will be bleached. When the printing is considered complete, the image may be fixed by a thorough washing. The washing removes any remaining cobalt compound and the layer thereafter has no light sensitivity.

Instead of the procedure outlined above, the emulsion of lead sulphide made as above by mixing Solutions A and B has added to it the cobalt compound. To accomplish this it is only necessary to add to the mixed emulsion (Solution A + Solution B) an equal volume of Solution C. The completed emulsion containing the cobalt salt is then coated and is ready for printing as before.

The single figure of the accompanying drawing shows in section and on an exaggerated scale a sensitive element embodying our invention.

In following out the process described it is, of course, necessary to add a sufficient quantity of cobalt salt to oxidize all of the lead sulphide to lead sulphate. Otherwise, it would not be possible to obtain clean whites in the print.

Any of the metal sulphides mentioned may be used interchangeably with lead sulphide. The quantity of sulphide used in an emulsion of the type described may be variable. The limits are set only by practical considerations. The coating made should have sufficient covering power to make a suitable print, and the coating must of course not be so thick or contain so much sulphide that the quantity of cobalt salt present is insufficient to bleach or oxidize the sulphide. The various metal sulphides are precipitated from suitable salts of the metals by methods

which differ little from that shown and which are well known.

The printing process as described requires the presence of a small amount of moisture for satisfactory results. For this reason we have included in the formula (Solution C) a little glycerin. The glycerin may be omitted if the paper is otherwise humidified before drying. Other hygroscopic agents may also be employed if they have no harmful effect on the coating.

We consider as included within our invention all modifications and equivalents coming within the scope of the appended claims.

What we claim is:

1. A photographic light sensitive element comprising a coating containing a heavy metal sulphide selected from the group consisting of lead sulphide, copper sulphide, bismuth sulphide, nickel sulphide, mercury sulphide and silver sulphide, and containing also a light sensitive oxidizing trivalent cobalt salt.
2. A photographic light sensitive element comprising a coating containing a heavy metal sulphide selected from the group consisting of lead sulphide, copper sulphide, bismuth sulphide,

nickel sulphide, mercury sulphide and silver sulphide, and containing also a light sensitive oxidizing trivalent cobalt salt selected from the group consisting of hexammine cobaltic chloride, nitroso-pentamine cobaltic chloride and tri-nitro-triamine cobalt.

3. A photographic light sensitive element comprising a coating containing lead sulphide and a light sensitive oxidizing trivalent cobalt salt.

4. A photographic light sensitive element comprising a coating containing lead sulphide and a trivalent cobalt salt selected from the group consisting of hexammine cobaltic chloride, nitroso-pentamine cobaltic chloride and tri-nitro-triamine cobalt.

5. A photographic light sensitive element comprising a coating containing a heavy metal sulphide selected from the group consisting of lead sulphide, copper sulphide, bismuth sulphide, nickel sulphide, mercury sulphide and silver sulphide, and containing also a light sensitive oxidizing trivalent cobalt salt and a hygroscopic material.

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