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PROCESS FOR PRODUCING AND DEVELOPING LIGHT-SENSITIVE PHOTOGRAPHIC LAYERS

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For some purposes it is necessary to produce substantially grainless photographic or light-sensitive layers or films, and for this purpose it has been proposed to sensitise a substantially grainless water-absorbent layer or film which is itself not sensitive to light or is quite insufficiently sensitive, for example, a gelatine layer, for recording an image. This problem arises, for example, in connection with layers or films which have a grating, especially in connection with U. S. application Serial No. 145,661 of February 23, 1950, which describes the manufacture of lenticular films having a high degree of light activity, and of which a special characteristic is the use of a support having a grating on both sides. For recording an image photo-active systems are proposed which consist of light-sensitive diazo compounds and silver or mercury salts (Kalle German Patent No. 640,233 and Philips Techn. Rundschau, Jahrgang 9, Nos. 3 and 10, pages 65-96 and 289-320).

The aforesaid sensitising solutions made with light-sensitive diazo compounds are known to have the disadvantage of a relatively high instability, so that it is necessary for copying purposes to expose and develop the sensitised material immediately after it has been dried.

The decomposition of the diazo solutions used leads to the formation of phenol derivatives having a reducing action, and these derivatives cause undesired fogging especially in colloid layers, when an intensifying development by means of unstable noble metal baths is used.

Sensitising solutions such as are described, for example, in German Patent No. 707,461, deposit considerable amounts of solid decomposition products in the course of 24 hours at room temperature and are therefore difficult to use in a copying establishment.

The present invention is based on the observation that substantially grainless water-absorbent layers or films for recording images can be sensitised by treating them with a solution of acid reaction which contains a complex iron salt and a silver salt.

It is obviously necessary that the water-absorbent layers or films used as starting materials in the present process should be sufficiently inert towards the sensitising solution and especially should contain no substances which themselves reduce silver salts or prevent such a reduction taking place owing to their oxidising action. Moreover these layers or films must be substantially grainless. Thus, there may be used as starting materials substantially grainless hydro-

philic colloid materials such as cellulose hydrate films or layers, for example, films which consist wholly of regenerated cellulose or films which consist of cellulose esters, such as cellulose acetate or mixed esters, such as cellulose acetate butyrate, which have been partially hydrolyzed, but preferably gelatine layers, and which films or layers may as stated above have a special form, for example, a lenticular grating, for producing special effects. The solutions used for sensitising in the present process may contain as a complex iron salt, especially a complex ferric salt, for example, a complex salt of an inorganic acid such as ferric ammonium sulphate, but especially complex salts of organic carboxylic acids, which may be mono-, di-, or polycarboxylic acids, which advantageously contain one or more hydroxyl groups. The iron bound in complex union may be present in an anion or a cation. As examples there may be mentioned hexa-aceto-hydroxo-triferric acetate nitrate, ferric ammonium oxalate, potassium diglycollato-ferrate, sodium dilactato ferrate, potassium disalicylato-ferrate and especially ferric complex compounds which contain as the organic carboxylic acid citric acid for example, the brown and especially the green ferric ammonium citrate.

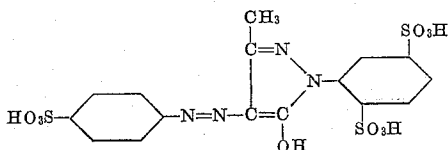
While certain of these complex compounds themselves exhibit an acid reaction, it may in other cases be necessary or advantageous in order to impart the acid reaction to the aforesaid sensitising solutions to add a free acid, for example, nitric acid, glycollic acid or citric acid.

In many cases it is also advantageous to add dyestuffs to the sensitising solutions described above. By the addition of suitable dyestuffs it is possible, for example, to increase the absorption of light in a desired region of the spectrum. Moreover, it is desirable in many cases to restrict the depth of penetration of the latent image into the water-absorbent layer or film, for example, in order to impart a very high resolving power to the light-sensitive layer or film, or, in the case of the above-mentioned double grating films, to reduce or avoid the danger of deformation of the lenticulations. For these purposes it is of advantage to add suitable dyestuffs, which then act as "damping dyestuffs."

The aforesaid "damping dyestuffs," in addition to possessing the desired optical properties, must sufficiently fulfil the condition of not leading to reactions with the other components of the sensitising solution, which reactions would adversely affect the present photo-chemical system, and depending on the purpose in view they must be

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easily removable. As "damping dyestuffs" there are suitable for example tartrazine or a pyrazolone dyestuff of the constitutional formula



The aforesaid acid-reacting solutions, which contain a complex iron salt of an organic carboxylic acid and a silver salt, usually produce precipitates shortly after they have been prepared or mixed, and these precipitates are harmful in the production of light-sensitive layers or films. It has been unexpectedly found that by clarifying the solution, for example, by filtering, decanting or centrifuging, stable solutions are obtained which when stored at room temperature in the dark for a few weeks remain unchanged without any appreciable alteration in their composition. In the present invention, therefore it is of advantage to start with solutions which have been subjected to a clarifying operation after standing for a short time.

The treatment of the water-absorbent layers or films with the aforesaid solutions may be carried out in a manner in itself known, for example, by immersion or impregnation by means of a roller or in any other manner, so that the water-absorbent layer or film is uniformly impregnated with the solution. The resulting layers or films are considerably more stable than the hitherto known layers or films produced with diazo compounds and can be stored, for example, for periods ranging from several days to weeks before they need be used.

The new photographic layers of films possess a resolving power (about 1000 lines per mm.) similar to that of layers or films prepared with metal diazo compounds. When used for copying they yield pale yellow to pale brown images.

The invention is also based on the observation that these images can be developed to neutral grey to black tints of good covering power by development with unstable noble metal solutions, for example, solutions which contain in addition to a silver salt, especially silver nitrate, a photographic developing substance, such as Metol, and also a weak acid for example tartaric acid. Unexpectedly development takes place with remarkable freedom from fog, especially in the case of light-sensitive layers or films which have not been stored for long periods, for example, for not more than 1-2 weeks.

The aforesaid intensifying development (see Eder, "Rezepte, Tabellen und Arbeitsvorschriften für Photokopie und Reproduktionstechnik," page 80, 1927) by means of unstable noble metal solutions is advantageously carried out by means of silver nitrate and a reducing component, such as ferrous sulphate, hydroquinone or parahydroxymethyl aniline, in an acid medium. As is generally known from the early literature of the colloid technique the silver nitrate may be used either in admixture with the reduction component or before or after the action of the component precipitating the silver. It is also possible, for example, to incorporate the silver nitrate necessary for development in the photo-sensitive layer or film, so that for the purpose of development it is necessary to treat the exposed layer or film only with the reducing component. It may often also be of advantage first to bring the ex-

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posed layer or film into contact only with water or slightly acidulated water, and intensify the resulting yellow image by one of the variants mentioned above to produce a useful image.

5 It is of advantage finally to wash the developed film well with distilled water, which may be carried out at room temperature or a slightly raised temperature depending on the degree of hardness of the colloid layer.

10 Images developed in the manner described above generally have a valuable neutral grey to black tint. Depending on the nature of the solution used for sensitisation the image may possess more or less pronounced half-tones. For certain copying purposes it is known to be important to obtain records which are practically free from half tones, and this condition can be fulfilled to a great extent in the present process. Further-
15 more it is possible that slight brownish borders may be present between the covered and uncovered parts in the record.

20 These borders which owing to their brownish tint are in some cases undesirable can be made to disappear, that is to say they can be converted to neutral grey or black, by treating the developed record with a solution of a metal salt of which the metal is more noble in the electromotive series than the metal which was used for development. As examples of such metal salts there may be mentioned the complex compounds of hydrohalic acids with noble metals such as gold and platinum, especially chloroplatinic acid.

25 The following examples illustrate the invention, the parts and percentages being by weight unless otherwise stated and the relationship of parts by weight to parts by volume being the same as that of the gram to the cubic centimetre:

Example 1

40 A layer consisting of light-tanned gelatine, for example, a double lenticular film made by the process of Dr. Gretener A. G., Zurich, is impregnated with a sensitising solution, which has been clarified by filtration after about 4 hours, of the following composition:

100 parts of distilled water,
10 parts of hexa-aceto-hydroxo-triferric acetate nitrate,
50 5 parts of silver nitrate,
0.2 part of a non-ion active wetting agent consisting of the condensation product of higher fatty alcohols with about 20 molecular proportions of ethylene oxide.

55 The wet film is dried in a dust-free current of air heated at 33-35° C., and is then used for copying.

60 The exposed film is developed by immersing it in a freshly prepared mixture of 40 parts by volume of an aqueous solution consisting of

4 per cent. of tartaric acid,
2 per cent. of Metol and
65 0.2 per cent. of a non-ion active wetting agent of the type described above and
2 parts by volume of a silver nitrate solution of 10 per cent. strength.

70 The development is complete in 4-5 minutes at 20-21° C. and the film may be dried after it has been washed in distilled water.

Example 2

75 Instead of the solution used in Example 1,

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there may be used a sensitising solution of the following composition:

110 parts of distilled water,
10 parts of ferric ammonium oxalate,
1 part of silver nitrate,
20 parts by volume of 2 N-nitric acid.

Before use the above solution is filtered to remove constituents which have precipitated.

Alternatively there may also be used instead of the solution mentioned in Example 1, a solution prepared as follows:

In 5 parts of distilled water containing 0.2 per cent. of a wetting agent described in Example 1 are dissolved 0.2 part of potassium diglycollato-ferrate and 0.1 part of glycollic acid. The clear solution is mixed with 5 parts of a silver nitrate solution of 10 per cent. strength, and then freed from small quantities of insoluble matter by filtration.

Finally, there may also be used a solution prepared as follows:

1 part of a solution of 22.4 per cent. strength of green ferric ammonium citrate in distilled water is mixed with 1 part by volume of a silver citrate solution of 10 per cent. strength.

In all the above cases the development may be carried out in the manner described in the third and fourth paragraphs of Example 1.

Example 3

A sensitising solution is prepared as follows:

52 parts of brown ferric ammonium citrate and 18.4 parts of citric acid

are dissolved together in 200 parts of distilled water. After dissolution 5 parts of an aqueous solution of 15 per cent. strength of a non-ion active wetting agent and 200 parts of a silver nitrate solution of 10 per cent. strength are added.

During mixing a small quantity of a colloidal precipitate separates, which is removed from the solution before use by centrifuging.

The resulting solution is used for impregnating the hardened gelatine side of a double grating film and the resulting film is dried at 33-36° C. in dust-free air.

The sensitising solution described above, during storage in the dark at room temperature precipitates only a trace of a dark coloured deposit in the course of the first few days, but, if it is then filtered, it remains absolutely clear for 14 days and facilitates the production of reproducible products.

The layers obtained in accordance with the foregoing examples can be stored in the dark for a long time, for example for a month at a room temperature of 18-20° C. without any crystalline deposits or chemical decomposition reactions being observed. It is important to maintain protective drying conditions and to store the products in a dry state.

Example 4

An image obtained in the manner described in Example 3 in conjunction with the developing procedure described in Example 1, and of which the black parts of the image are surrounded by a fine yellow to yellow brown border, is treated for 10-20 seconds with an aqueous solution of 2 per cent. strength of chloroplatinic acid, and then thoroughly washed with distilled water. By this treatment the coloured borders are con-

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verted into neutral grey to black parts of the image.

Example 5

26 parts of brown ferric ammonium citrate, 9.2 parts of citric acid, 8.0 parts of the salt-free azo dyestuff obtained by coupling 1-(2:5-disulphophenyl)-3-methyl-5-pyrazolone with diazotized sulphanilic acid with the addition of pyridine; and 1.0 part of a non-ionic wetting agent of the type of a fatty alcohol-polyethylene oxide condensation product are dissolved in 100 parts of distilled water.

To the resulting mixture is added a solution of 10 parts of silver nitrate in 100 parts of distilled water, and the reaction mixture, from which an amorphous precipitate then separates, is stored at room temperature.

Before use the stored sensitising solution is freed from the original precipitate and from the deposit subsequently formed during standing by centrifuging.

The sensitising solution so obtained can be used instead of that described in Example 1, 2 or 3.

Example 6

A cellulose acetate butyrate film, which is provided with a cylinder grating, is hydrolysed on its smooth surface about 4 μ deep with an alcoholic solution of caustic soda by placing it for 4 minutes on the surface of the hydrolysing solution.

For preparing the hydrolysing solution 16 grams of sodium hydroxide are dissolved in 20 cc. of distilled water, and the whole is made up to 100 cc. by the addition of alcohol of 96 per cent. strength. The solution is clarified by filtration and then used immediately.

After the hydrolysis, the film is freed from excess of caustic soda by washing in distilled water for 10 minutes and dried in the air. It is sensitised with the solution described in Example 3 by immersion for about 1 minute and washing the side of the film carrying the grating with distilled water.

The sensitised film is dried at 33-34° C. for 10-20 minutes by passing dust-free air over it.

In order to obtain favourable or constant copying values, and also to increase the threshold sensitivity, the exposed film is conditioned, before development, in a room having a temperature of 20-22° C. and a relative humidity of 90-95 per cent. for 1/4-1/2 hour.

The same conditioning treatment may be applied to the layers used in Examples 1, 2, 3 and 5. Generally speaking, an atmosphere of high water content, such as above 60 per cent. relative humidity and preferably about 85 to 95 per cent. relative humidity should be used.

What is claimed is:

1. A process for producing photographic records, which comprises impregnating a substantially grainless hydrophilic colloid layer supported by a substantially grainless transparent film material, with a clarified acidulated solution which contains a complex ferric salt of an aliphatic hydroxy-carboxylic acid and a water soluble silver salt, exposing the sensitized layer and developing it with a solution of Metol, a weak acid, silver nitrate and a non-ionic wetting agent.

2. A process for producing photographic records, which comprises sensitizing a substantially grainless hydrophilic colloid layer on a transparent grainless film support with a clarified solution containing hexa acto-hydroxo-triferric ace-

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tate nitrate, silver nitrate and a non-ionic wetting agent, exposing the sensitized layer and developing it with a solution of Metol, tartaric acid, silver nitrate and a non-ionic wetting agent.

3. A process as in claim 2 wherein the sensitized layer is conditioned after exposure and before development in an atmosphere of at least 60% relative humidity.

4. A process as in claim 2 wherein the sensitizing solution contains a silver latent image sensitizing dye which restricts the depth of penetration of said latent image into said hydrophilic layer.

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