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DEVELOPMENT OF PHOTOGRAPHIC EMULSIONS

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8 Claims. (Cl. 95—88)

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This invention relates to photography and particularly to a method for the "dry" processing of photographic emulsions.

In Yackel, Leermakers and Staud U. S. application Serial No. 500,924, filed concurrently herewith, a process is described of developing photographic emulsions containing developing agents, by the application of vapors of ammonia or other alkali. In that process it is necessary to develop the emulsion in a closed container so that the vapors of ammonia or other alkali are confined to the material being treated. It is frequently inconvenient to develop an emulsion in this way since the process necessitates the use of a suitable apparatus for confining the alkaline vapors to the material being processed.

It is, therefore, an object of the present invention to provide a method for developing photographic emulsions containing developing agents without the use of special apparatus. A further object is to provide a method for developing exposed photographic emulsions without the application of alkaline vapors. A still further object is to provide a novel photographic material which may be processed conveniently by "dry" development. Other objects will appear from the following description of our invention.

These objects are accomplished, according to the broader aspects of our invention, by incorporating in a silver halide emulsion a photographic developing agent and a nitrogen compound capable of generating an amine, and treating the exposed photographic material with steam or water vapor. This combination of ingredients produces a material which is suitable for use in "dry" processing of the emulsion, that is, processing without immersing the exposed photographic material in a liquid bath and, therefore, secures the advantages referred to in the Yackel, Leermakers and Staud application Serial No. 500,924. These advantages include the rapid development of the photographic material without resorting to long washing and drying steps.

According to our invention there is incorporated in a silver halide photographic emulsion, such as a gelatino-silver halide photographic emulsion, a photographic developing agent and a nitrogen compound capable of generating an amine. The developing agent may be any suitable known compound such as hydroquinone, Elon, Amidol, or p-phenylenediamine. The nitrogen compound capable of generating an amine, may be a compound which generates ammonia or an amine on heating, decomposition or

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reaction with other compounds. The amines or ammonia do not cause development of the emulsion in the dry state but, in the presence of water, development of the exposed emulsion is brought about. In the case of ammonia there is sometimes sufficient water in the coated emulsion to effect development but generally with the amines which are not decomposed to form ammonia, water must be added to effect development. Development can, therefore, be accomplished by the application to the exposed material of steam or water vapor.

The amines incorporated in the emulsion may be soluble or insoluble in water. The water-soluble amines may be added directly to the emulsion but the water-insoluble compounds are preferably dissolved in a water-insoluble, water-permeable solvent which is then dispersed in the emulsion. When incorporated in this way, the water-insoluble amines do not react on the silver halide until they are released by the action of the steam and the emulsion may, therefore, have a greater speed than when the water-soluble amines are incorporated directly in the emulsion. When the emulsion is acted on by steam, the amine is released from the solvent by what amounts to steam distillation, and thereby increases the alkalinity of the emulsion to the point where development of the layer is produced.

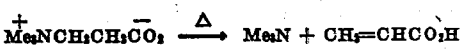
Water-insoluble amines which may be employed according to our invention, include diisoamylamine, n-heptylamine, benzylamine and β-amino-n-octane. These compounds are dissolved in a water-insoluble, water-permeable solvent such as butyl phthalate, ethyl sebacate, tri-o-cresyl phosphate, n-amylsuccinate, butyl benzoate or isoamylsulfone. Other water-insoluble, water-permeable materials such as those referred to on pages 2 and 3 of Jelley and Vittum U. S. Patent 2,322,027, granted June 15, 1943, may be employed.

The following water-soluble amines may be employed:

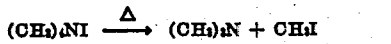
Ethylenediamine
Ethanolamine
Guanidine carbonate
Guanidine hydrochloride
Guanidine laurate
Guanine hydrochloride
2-amino-2-ethyl-propanediol
Formamide
Adenine sulfate
Hexamethylenetetramine
Urea

The following compounds, which generate ammonia or amines on heating or by reaction with other compounds, may be employed, the reaction by which the ammonia or amines are produced being indicated below. While these are the reactions indicated in chemical textbooks, it is improbable that these are the only products produced under the conditions of our invention.

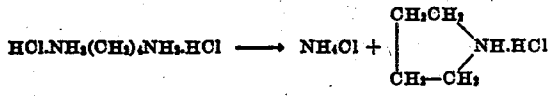
Betaines



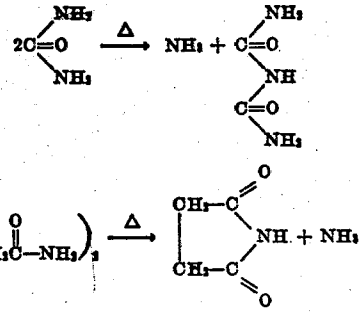
Tetramethylammonium iodide



Diaminobutane.2HCl



Urea



The following examples illustrate methods of preparing emulsions according to our invention:

Example 1

To 200 cc. of a gelatino-silver bromoiodide emulsion there are added the following ingredients:

	Cc.
Chrome alum (5.5% solution)	9
2 - (p - dimethylaminophenyliminomethyl) - benzothiazole ethoethylsulfate (desensitizer) (0.1% solution)	11
Hydroquinone (10% solution)	3
Sodium sulfite (10% solution)	1.5
Soap bark extract	16
Dispersion of β-amino-n-octane	10

The dispersion of β-amino-n-octane is prepared by mixing the following ingredients:

β-Amino-n-octane	cubic centimeters	5
Ethyl sebacate	do	25
Gelatin (10% solution)	do	65
Water	do	60
Alkanol B	grams	1

This mixture is passed five times through a colloid mill to effect a dispersion of the ethyl sebacate containing the amine in the gelatin solution.

The emulsion was coated on a suitable support such as paper, glass or film, exposed to light and then heated for three minutes in a stream of steam and dried on a hot plate at moderate temperature for about one minute. This gave a very good image with little development outside the exposed areas.

Example 2

An emulsion was prepared in the same manner as described in Example 1, using a dispersion of n-heptylamine instead of a dispersion of β-amino-n-octane, the n-heptylamine being incorporated in the dispersion in an amount of 5 cc. and 10 cc.

of the dispersion being added to 200 cc. of emulsion.

Example 3

An emulsion containing a water-soluble amine was prepared as follows:

To 200 cc. of gelatino-silver halide emulsion there was added the following solution:

	Cc.
Chrome alum (5.5% solution)	9
2 - (p - dimethylaminophenyliminomethyl) - benzothiazole ethoethylsulfate	11
Hydroquinone in methyl alcohol (10% solution)	3
Sodium sulfite (10% solution)	1.5
Urea (10% solution)	10

Example 4

An emulsion containing a water-soluble amine was prepared by adding to 200 cc. of a gelatino-silver halide emulsion, the following solution:

	Cc.
Chrome alum (5.5% solution)	9
2 - (p - dimethylaminophenyliminomethyl) - benzothiazole ethoethylsulfate (0.1% solution)	11
Hydroquinone in methyl alcohol (10% solution	3
Sodium sulfite (10% solution)	1.5
Guanine hydrochloride (10% solution)	10

After adding this mixture to the emulsion, the emulsion was adjusted to pH 6 before coating.

While development with steam as described above produces a satisfactory photographic image, the image thus produced is not permanent. Development proceeds slowly upon exposure of the steam developed image to artificial light and more rapidly upon exposure to sunlight. This is caused by gradual development of the residual silver halide by the developing agent remaining in the emulsion and may be overcome by treatment of the steam developed material with acid vapors or with an iodizing material. The following procedures are available.

1. The developed material may be treated with vapors of an acid such as hydrochloric acid.

2. The residual silver halide may be iodized by bathing the developed material for one to two minutes in a 10% solution of potassium iodide or in a 10% potassium iodide solution containing 3% of sodium bisulfite. This prevents further development even in direct sunlight by converting the silver halide to silver iodide.

3. The silver halide may be iodized by incorporating in the dispersion of the amine or in the emulsion a dispersion of an alkyl or aryl iodide. n-Butyl, ethyl, secondary butyl, tertiary butyl or other alkyl iodide may be used to iodize the residual silver halide. The iodides vary in their reactivity and a wide choice is available. The dispersion of iodide need not be incorporated directly in the emulsion but may be coated over or under the emulsion layer. Upon heating with steam, the iodide is driven out of the dispersed particles and reacts with the silver halide. The dispersion of the iodide may be made as follows:

n-Butyl iodide	grams	10
Butyl phthalate	do	20
Gelatin (10% solution)	cubic centimeters	40
Water	do	30
Alkanol B	grams	0.3

This mixture is passed three times through a colloid mill in order to effect a dispersion of the iodide and butyl phthalate in the gelatin.

The introduction of the alkyl or aryl iodide as a dispersion or as part of the dispersion of the amine is necessary because if it were added in solution to the emulsion it would immediately react with the silver halide and thus render it undevelopable after exposure. By adding the alkyl or aryl iodide as a dispersion, it does not come in contact with the silver halide except in the presence of considerable quantities of water vapor and the solution of the iodide and its subsequent reaction with silver halide is thus delayed until after the development has been completed.

4. The iodide may be introduced in the steam after development. For example, after exposure and development by steam as described above, an alcoholic solution of iodide is introduced in the steam to effect a conversion of the silver halide to silver iodide. A fairly active organic iodide such as tertiary butyl iodide or allyl iodide may be used for this purpose. However, since these compounds are quite unstable, a more convenient compound is hexamethylenetetramine allyl iodide or other quaternary ammonium salt of such active iodide. This allows easier handling of the material and injurious by-products such as hydriodic acid or iodine which would oxidize the developed image are less likely to be present. After treatment with volatile iodides in this way, the print is dried quickly, for example, on a hot plate as described above.

Our process of development is useful in the production of copies of line drawings where a number of copies are needed in a minimum of time or where the copies need not be stable over long periods of time. The advantage of using steam to introduce the moisture necessary for development is that the paper base or other support does not become wet during processing, washing is eliminated and drying is accomplished in a few seconds.

It will be understood that the modifications and examples described are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. The method of developing an exposed silver halide layer containing a photographic developing agent and an excess of an organic nitrogen compound capable of generating a volatile amine upon application of steam, which comprises subjecting said exposed layer to the action of steam.

2. The method of developing an exposed gelatino-silver halide emulsion layer containing a silver halide developing agent and an excess of an ammonia-generating organic compound, which comprises subjecting said exposed layer to the action of steam for a sufficient length of time to generate ammonia from said organic compound and to produce a visible image in said layer.

3. The method of developing an exposed gelatino-silver halide emulsion layer containing

a silver halide developing agent and an excess of an ammonia-generating organic compound, which comprises subjecting said exposed layer to the action of steam for a sufficient length of time to generate ammonia from said organic compound and to produce a visible image in said layer and then treating the layer with acid vapors for a short period of time.

4. The method of developing an exposed gelatino-silver halide emulsion layer containing a silver halide developing agent and an excess of an ammonia-generating organic compound, which comprises subjecting said exposed layer to the action of steam for a sufficient length of time to generate ammonia from said organic compound and to produce a visible image in said layer and then iodizing the undeveloped silver halide in the layer.

5. The method of developing an exposed gelatino-silver halide emulsion layer containing a silver halide developing agent and an excess of an ammonia-generating organic compound, which comprises subjecting said exposed layer to the action of steam for a sufficient length of time to generate ammonia from said organic compound and to produce a visible image in said layer, and then treating said layer with vapors of a volatile iodide to convert the remaining silver halide to silver iodide.

6. A photographic emulsion capable of being developed by the application of steam only, comprising a gelatino-silver halide emulsion containing a photographic developing agent and having dispersed therein particles of a water-insoluble, water-permeable liquid containing a water-insoluble amine capable of generating a volatile amine and thereby increasing the alkalinity of the emulsion upon application of steam to the emulsion.

7. The method of forming a silver image in a silver halide emulsion layer without immersing said layer in a liquid, which comprises incorporating in a slow silver halide emulsion a silver halide developing agent, and an organic nitrogen compound capable of generating a volatile amine upon application of steam, coating said emulsion on a support, exposing said emulsion to light, and subjecting said exposed emulsion to the action of steam to produce a silver image therein.

8. The method of forming a silver image in a silver halide emulsion layer without immersing said layer in a liquid, which comprises incorporating in a silver halide emulsion a silver halide developing agent, a desensitizer, and an organic nitrogen compound capable of generating a volatile amine upon application of steam, coating said emulsion on a support, exposing said emulsion to light, and subjecting said exposed emulsion to the action of steam to produce a silver image therein.

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