Patented July 30, 1946 2,404,774

UNITED STATES PATENT OFFICE

2,404,774

PHOTOGRAPHIC DEVELOPING PROCESS

Fritz Dersch, Binghamton, and Newton Heimbach, Johnson City, N. Y., assignors to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application July 2, 1943, Serial No. 493,254

19 Claims. (Cl. 95—88)

1

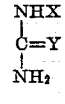
This invention pertains to a process for increasing the speed of development of a silver halide emulsion.

Photographic films having silver halide emulsions of sufficiently high speed and, when developed with ordinary developers, yielding negatives with silver grains that are not objectionably large for ordinary photographic purposes, have been developed and are now well known to the art. It has been observed that some difficulty is often encountered in obtaining proper gradation upon development of such films especially during optimum developing time. The principal development appears to be at the surface of the exposed layer due probably to the resistance of the gelatin emulsion to penetration by the developer solution. Increasing the developing time in order to promote deeper penetration into the exposed layer increases the fog characteristic. Accordingly, it is an object of this invention to provide a process for increasing the speed of development or improving the gradation or contrast of known gelatino silver halide films. It is a further object to provide a developer which will effect this result.

It is well known that there is a loss of activity on the part of developing agents commonly used in the development of photographic films during continued use of the developing solution. As the activity of the developer decreases on approaching exhaustion, the time of development and hence the fog characteristics become the greater. Accordingly, it is still another object of this invention to provide a process for revivifying or increasing the activity of a partially exhausted developer.

It is often a disadvantage to carry out the development with commonly used developers at their required developing temperature of 65° F. (18° C.). It is, therefore, a further object of this invention to provide a process for development with all common developers at lower temperatures.

It has now been found that the development of exposed gelatino silver halide emulsions in the presence of a compound of the general formula



wherein Y represents a member of the group consisting of oxygen and NH, X represents a member of a group consisting of hydrogen, methyl, and allyl radicals and cyanogen, but cyanogen only when Y represents NH, considerably decreases the developing time required for reaching

2

a given degree of contrast or, if normal developing time is employed, produces the effect of higher speed and better contrast on the developed film. These results are accomplished by adding such compounds to the developing solution used for development of the exposed gelatino silver halide emulsion. Without in any way limiting our invention to any particular theory as to the mechanism of the action of said compounds in the developing process it is suggested that they have a softening or swelling action which permits the developer to reach the silver halide grain in a shorter time or permits the developer to penetrate more deeply in a given length of time into the emulsion and thus produce greater contrast.

Other materials, such as substantial amounts of sodium hydroxide and substantial amounts of thiourea or thiocyanates are known to have a marked softening effect on gelatin, but their function in the presence of a gelatin medium is somewhat obscure due to the lack of sufficient knowledge of the chemical structure of the gelatin itself. It is believed, however, that at least a temporary chemical alteration of the gelatin structure occurs which is accompanied by a marked change in the physical properties such as lowering of the melting point and setting point, and such softening agents also have undesirable specific effects on the photographic emulsion. Sodium hydroxide, for instance, has a tendency to fog the emulsion. Thiourea or thiocyanates, being silver halide solvents, also fog the photographic emulsion. Urea and the other compounds used in accordance with the present invention are free from these undesirable effects. The swelling or softening effect which they exert occurs only during the time of contact of the developing solution with the gelatin. There is no permanent swelling effect and upon removal of the emulsion from the developing solution and washing, the original physical properties of the gelatin are substantially restored.

For simplicity of expression the following general description of the invention will be made in connection with urea as a specific embodiment, and it is to be understood that any of the other compounds falling within the above general formula may be employed in place thereof. When the urea is added to the developer for the development of any ordinary gelatino silver halide emulsion, it is preferable to make the addition just prior to use of the developer. This is particularly so when using those developers which are high in alkalinity and low in sulfite since the stability of such developers is impaired by long contact with urea. Developers which contain

the least possible amount of alkali and the highest possible amount of sulfite are rather stable in the presence of urea and hence are not so apt to be subject to this decomposition.

The increase in speed of development and greater contrast obtained by developing a gelatino silver halide emulsion in the presence of urea are not dependent upon the use of any particular type of developer. The developers may be simple hydroquinone developers which contain hydroquinone, potassium metabisulfite and potassium bromide, or they may be the metol-hydroquinone type of developer which contain p-methylaminophenol, sodium sulfite, sodium bisulfite, hydroquinone, sodium carbonate, and potassium bromide or they may have a composition of a so-called borax developer which contains p-methylaminophenol, sodium sulfite, hydroquinone, borax and potassium bromide. In short, the effect is obtainable with practically all types of developers used for developing the latent image of an exposed silver halide emulsion. The developing time of any such developer can be decreased from 20 to 30% by the addition of from 50 to 150 grams of the urea to 1 liter of the developing solution.

The retarded speed of development or decrease of gradation obtainable in a given time for a partially exhausted developing solution can be increased by the addition of urea to such a developer. Replenishment or revivification of a partially exhausted developer where normal gradation and developing speed have gradually decreased with the exhaustion is thereby effected. For revivifying partially exhausted developer solutions, from 50 to 150 grams of the urea per liter of the exhausted developer solution may be added, or as little as 40 grams dicyandiamide may be added. A substantial prolonging of the normal life of the developer is obtained and it is possible to develop almost as many photographic films in such a revived developer as were developed in the original solution before it became exhausted. In the case of such exhausted developers, the decrease in developer activity is believed to be at least partially due to the tanning effect of the oxidation products of the organic compounds used in the developers. This tanning effect of said oxidation products is believed to be counteracted by the presence of the urea and the penetration of the developer chemicals into the emulsion layer is facilitated.

It is the general practice to develop silver halide emulsions at temperatures of not less than 65° F. (18.34° C.) since development at lower temperatures with commonly used developing agents cannot be carried out successfully. However, it is often necessary to carry out the development under adverse atmospheric conditions or other influencing factors which make difficult the maintenance of the optimum developing temperature. When adding as much as 300 grams of urea to a liter of developing solution, developing temperature of as low as 45° F. (7.22° C.) can be used without any impairment of the developed image. Smaller amounts of urea can be used, depending upon the developing temperature desired. Thus an addition of 150 grams of urea per liter of developing solution gives the same development at 55° F. as is obtained without addition of urea at 65° F.

The following examples may serve to illustrate the invention which, however, is not limited thereto. The parts are by weight unless otherwise indicated.

Example I

A developing solution was made up as follows:

Hot water (125° F. or 52° C.)	cc	750
Metol (p-methylaminophenol)	g	3.5
Sodium sulfite, anhydrous	g	60
Hydroquinone	g	9
Sodium carbonate, monohydrated	g	40
Potassium bromide	g	2
Water to make	liters	1

Two separate batches of this developer were made up, one being used without further additions or dilution as a "blank." To the other there was added 300 g. of urea. Exposed X-ray films having the same degree of exposure were developed in each of the solutions. In the case of the "blank" solution, development was carried out at 65° F. (18.34° C.). In the case of the solution having the addition of 300 g. of urea, development was carried out at 45° F. (7.22° C.). The time of development was the same in both cases. It was observed that the film developed at the lower temperature in the developer containing the urea was developed to the same contrast as the film which was developed at the normal temperature in the "blank" developer.

Example II

A developing solution was made up as follows:

Hot water (125° F. or 52° C.)	cc	750
Metol (p-methylaminophenol)	g	0.8
Sodium sulfite, anhydrous	g	45
Hydroquinone	g	1.2
Sodium carbonate, monohydrated	g	8
Potassium metabisulfite	g	4
Potassium bromide	g	1.5
Water to make	liters	1

Two separate batches of this developer were made up; one of these was used without further additions or dilution to develop an exposed silver halide high-speed film having a high orthochromatic sensitization (the "blank" solution). To the other batch there were added 100 g. of urea and the resulting developer was used without further dilution to develop an exposed silver halide film of the same type.

The development in both cases was at 68° F. (20° C.) and under usual conditions of agitation. The time of development in the case of the "blank" developer was seven minutes and in the case of the developer containing the urea, six minutes. The two films were washed, fixed and dried in the usual manner and under the same conditions.

The film developed in the developer solution containing urea showed a better contrast than that developed in the solution which did not contain urea. A saving of from 15 to 20% in developing time is therefore apparent as well as an improved result when developing in the presence of urea.

Example III

A developing solution was made up as follows:

Hot water (125° F. or 52° C.)	cc	750
Metol	g	1.5
Sodium sulfite, anhydrous	g	80
Hydroquinone	g	3
Borax	g	3
Potassium bromide	g	0.5

Two separate batches of this developer were made up, one being used as a "blank" as in the case of Example I. To the other there was added 150 g. of methyl urea. The same type of ex-

posed film and the same procedure or development as recited in Example I were used. The development time in the case of the "blank" of this developing solution was seven minutes and in the case of the developing solution containing methyl urea, five minutes. A better contrast was again obtained when developing in the presence of methyl urea. The saving in developing time achieved was from 25 to 30%.

Example IV

A developing solution of the following composition was made up:

Hot water (125° F. or 52° C.)	cc	750
Metol	g	3.5
Sodium sulfite, anhydrous	g	60
Hydroquinone	g	9
Sodium carbonate, monohydrated	g	40
Potassium bromide	g	2
Water to make	liters	1

Two separate batches of this developer were made up, one being used without further additions or dilution as a "blank." To the other there was added 100 g. of urea. Exposed X-ray films having the same degree of exposure were developed in each of the solutions. The development in both cases was at 65° F. (18.34° C.). The time of development in the case of the "blank" developer was five minutes and in the case of the developer containing urea, four minutes. This represents a saving in developing time of from 20 to 25%. It was also observed that the film developed in the developer solution containing urea showed a better contrast than that developed in the "blank" solution.

Example V

A developing solution having the following composition was made up:

Hot water (125° F. or 52° C.)	cc	750
Metol	g	1.5
Sodium sulfite, anhydrous	g	45
Sodium bisulfite	g	1
Hydroquinone	g	3
Sodium carbonate	g	6
Potassium bromide	g	0.8

Exposed strips of silver halide high-speed film having a high orthochromatic sensitization were developed in the above developing solution for seven minutes each at 68° F. (20° C.). When the solution began to lose strength and the desired degree of development was no longer obtained in the said developing time, 100 g. of urea were added to the solution. The resulting developing solution was then reused to develop the same number of films exposed under the same conditions as were developed in the original developing solution. The same developing time of seven minutes was used on the films developed after addition of the urea and the same degree of development was obtained as was obtained in the case of the films developed prior to exhaustion of the original solution.

Example VI

A developing solution having the following composition was made up:

Hot water (125° F. or 52° C.)	cc	750
Metol	g	3.5
Sodium sulfite, anhydrous	g	60
Hydroquinone	g	9
Sodium carbonate, monohydrated	g	40
Potassium bromide	g	2
Water to make	liters	1

Exposed strips of silver halide high-speed film having a high orthochromatic sensitization were developed in this developer for seven minutes each at 68° F. (20° C.). When the solution began to lose strength and the desired degree of development was no longer obtained in the same developing time 40 g. of dicyandiamide were added to the solution. The resulting developing solution was then reused to develop the same number of films exposed under the same conditions as were developed in the original developer. The same developing time was used for the films developed after addition of the dicyandiamide and the same degree of development was obtained as was obtained in the case of the films developed prior to exhaustion of the original developer.

Having now fully set forth and described our invention and having illustrated the best manner in which to perform it by specific examples, what we claim as new and desire to have secured by Letters Patent is:

1. A process for the development of a gelatino silver halide emulsion which comprises developing such an emulsion in a developer solution containing at least 50 grams urea per liter.

2. A process for the development of a gelatino silver halide emulsion which comprises developing such an emulsion in a developer containing a compound of the general formula



wherein Y represents a member of the group consisting of oxygen and NH, X represents a member of a group consisting of hydrogen, methyl, and allyl radicals and cyanogen, but cyanogen only when Y represents NH, in a concentration of from about 50 to 150 grams to 1 liter of developing solution.

3. A process for the development of a gelatino silver halide emulsion which comprises developing such an emulsion in a developer containing urea in the proportion of from about 50 to 150 grams to 1 liter of developing solution.

4. A process for the development of a gelatino silver halide emulsion which comprises developing such an emulsion in a developer containing 150 grams of methyl urea to 1 liter of developing solution.

5. A process of revivifying a partially exhausted photographic developing solution which comprises adding to the partially exhausted developing solution a compound of the general formula



wherein Y represents a member of the group consisting of oxygen and NH, X represents a member of a group consisting of hydrogen, methyl, and allyl radicals and cyanogen, but cyanogen only when Y represents NH in the proportion of at least 40 grams per liter of developing solution when the compound is dicyandiamide and at least 50 grams per liter of developing solution when the compound is any other member of the group.

6. A process of revivifying a partially exhausted photographic developing solution which comprises adding urea to the partially exhausted developing solution in the proportion of from about 50 to 150 grams of urea per liter of solution.

7. A process of revivifying a partially exhausted photographic developing solution which com-

prises adding dicyandiamide to the partially exhausted developing solution in the proportion of at least 40 grams of dicyandiamide per liter of solution.

8. A process for the development of a gelatino silver halide emulsion which comprises developing such an emulsion at temperatures below 65° F. in a developer containing 50 to 300 grams per liter of a compound of the general formula



wherein Y represents a member of the group consisting of oxygen and NH, X represents a member of a group consisting of hydrogen, methyl, and allyl radicals and cyanogen, but cyanogen only when Y represents NH.

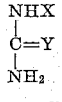
9. A process for the development of a gelatino silver halide emulsion which comprises developing such an emulsion at a temperature of 45° F. in a developer containing 300 grams per liter of urea.

10. A photographic developer composition comprising hydroquinone and 50 to 300 grams per liter of a compound of the general formula



wherein Y represents a member of the group consisting of oxygen and NH, X represents a member of a group consisting of hydrogen, methyl, and allyl radicals and cyanogen, but cyanogen only when Y represents NH.

11. A photographic developer comprising p-methylaminophenol, hydroquinone and a compound of the general formula



wherein Y represents a member of the group consisting of oxygen and NH, X represents a member of a group consisting of hydrogen, methyl, and allyl radicals and cyanogen, but cyanogen only when Y represents NH, in the proportion of from 50 to 150 grams per liter of developing solution.

12. A photographic developer comprising p-methylaminophenol, hydroquinone and urea in the proportion of from 50 to 150 grams urea to 1 liter of developing solution.

13. A photographic developer comprising p-methylaminophenol, hydroquinone, and methyl urea in the proportion of from 50 to 150 grams methyl urea to 1 liter of developing solution.

14. A photographic developer comprising p-methylaminophenol, hydroquinone and dicyandiamide in the proportion of about 50 grams of dicyandiamide to 1 liter of developing solution.

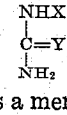
15. A photographic developer comprising p-methylaminophenol, hydroquinone and urea in the proportion of 300 grams of urea to 1 liter of developing solution.

16. The process which comprises developing a gelatino silver halide emulsion in a solution containing a developer, an alkali metal sulfite in a concentration greater than 45 grams per liter and an alkali equivalent to not greater than 40 grams per liter sodium carbonate and at least 50 grams per liter of a compound of the general formula



wherein Y represents a member of the group consisting of oxygen and NH, X represents a member of the group consisting of hydrogen, the methyl and allyl radicals and cyanogen, but cyanogen only when Y represents NH.

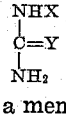
17. The process which comprises developing a gelatino silver halide emulsion in a solution comprising a developer, at least 45 grams sodium sulfite per liter, an alkali equivalent to not greater than 8 grams per liter sodium carbonate, and at least 50 grams per liter of a compound of the general formula



wherein Y represents a member of the group consisting of oxygen and NH, X represents a member of the group consisting of hydrogen, the methyl and allyl radicals and cyanogen, but cyanogen only when Y represents NH.

18. The process which comprises developing a gelatino silver halide emulsion in a developer solution containing a developer, an alkali metal sulfite in a concentration greater than 45 grams per liter and an alkali equivalent to not greater than 40 grams per liter sodium carbonate and at least 50 grams per liter of urea.

19. The process which comprises developing an exposed photographic film in a solution comprising a developer, at least 45 grams sodium sulfite per liter, an alkali equivalent to not greater than 8 grams per liter sodium carbonate, and at least 50 grams per liter of a compound of the general formula



wherein Y represents a member of the group consisting of oxygen and NH, X represents a member of the group consisting of hydrogen, the methyl and allyl radicals and cyanogen, but cyanogen only when Y represents NH.

FRITZ DERSCH.
NEWTON HEIMBACH.