

UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC DEVELOPER

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mesne assignments, to Hutchison Fine Grain
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6 Claims. (Cl. 95—88)

My present invention includes subject matter set forth in my earlier application Ser. No. 711,995, filed Feb. 19, 1934, of which it is in part, a continuation. The invention relates to photographic developers particularly adapted for developing photographic films and plates of the high speed type, and more particularly those where the negative is to be greatly enlarged as, for instance, in motion picture theatres where the picture on the screen is of enormous area as compared with the film. As is well known, the picture on the film is in the form of a silver coating of variable density and this coating is in the form of grains formed on the film by reaction of the developer on the light-exposed parts of the emulsion. When sufficiently magnified by projecting the picture through the negative, the grains become noticeable and, other things being equal, the larger the grains the less faithful will be the reproduction of the relatively minor values in shade tones, and the more the general sharpness of the picture will be blurred.

In the present state of the art, it is not difficult to make films having emulsions that are sufficiently high speed when used with the ordinary developer and which yield negatives with silver grains that are not objectionably large for ordinary photograph purposes; nor is it difficult to get fine grain silver deposits if the emulsion speed be sufficiently lowered, that is, if time of exposure be sufficiently increased; but prior attempts to combine these qualities have resulted in serious loss in emulsion speed and lack of commercial adaptability, except in the case of developers that have characteristic reactions similar to those of the one generally known as Eastman D76 borax developer, which is now regarded as standard for use in the development of motion picture negatives and which produced a relatively fine grain without substantial loss of emulsion speed.

It is a well-known characteristic, typical of all such conventional developers for high speed emulsions, including not only the above Eastman "borax developer", but also those which Eastman calls "M-Q" type; that the kinds, percentages and concentrations of the various constituents are carefully balanced with respect to one another; that is to say, for a liter, or other given volume of water, the silver halide grain developer, such as hydroquinone, will be in quantity and concentration suitable for reducing the silver halide of the emulsion; the preserving constituent, such as sodium sulfite, will be in quantity and concentration suitable for the halide grain

developer; and the alkaline accelerator, borax or sodium carbonate, will be likewise in balance for the halide grain developer and the sodium sulfite. If the halide grain developer includes metol as well as hydroquinone, the balance between them is governed by the fact that metol is high speed and gives detail in the shadows with low over-all density, while hydroquinone is low speed and builds up density over all parts of the negative. Said conventional developers for high speed emulsions are characterized by high sodium sulfite concentration, as for instance, 70 to 100 grams or more per liter; also by alkalinity not exceeding that which will fog the negative to an objectionable extent.

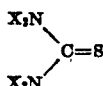
I have discovered as developers of this type, that if the alkalinity happens to be, or can be made low enough without destroying the desired accelerator effect, the addition of thiourea ($\text{CH}_4\text{N}_2\text{S}$) in concentration of 0.01 gram to 0.04 gram per liter; or of ammonium sulfocyanate (which is another form of $\text{CH}_4\text{N}_2\text{S}$), in concentrations of 0.5 to 3 grams per liter, give marked reduction of size of the silver grains in the negative, without causing prohibitive fog; and this notwithstanding the fact that such added reagents are like alkalinity in tending toward fog if used in excess. For thiourea, the balanced solution must not exceed alkalinity represented by 2 grams to 15 grams of borax per liter; and for ammonium sulfocyanate, 0.25 gram to 3 grams of sodium carbonate. Specific quantities within the above limits depend on the normal developing characteristics of the complete developer.

The specific object of the invention is to improve upon these relatively successful fine grain developers so as to secure a much finer grain in the negative without any material loss in emulsion speed.

The above relatively successful developers are more or less conventional as concerns employment of metol and hydroquinone, usually about 2 grams of the former and 5 grams of the latter per 1,000 grams (1 liter) of water; but as concerns the production of fine grains with which my present invention is concerned, the more important characteristics are the relatively high concentration of sodium sulfite and the relatively small percentage of alkaline accelerator. The sodium sulfite may be as high as 100 grams and the alkaline accelerator (borax) as low as 2 grams per 1,000 grams of water. In said developers the production of the fine grains is due primarily to the powerful solvent action of this highly concentrated sodium sulfite on the silver

halogen grains of the negative emulsion; and an essential contributing factor is the weakness of the accelerating action due to the relatively great dilution of the alkaline constituent, in this case borax. This characteristic small alkalinity gives sufficient time for the solvent action of the concentrated sodium sulfite to become effective in forming the silver in fine grains. The use of borax in this connection is only a convenience, because a similarly effective weak alkalinity could be obtained by employment of a proportionally less amount of sodium carbonate, say $\frac{1}{2}$ as much.

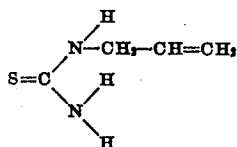
I have discovered that developers having the above characteristic concentration of silver salt solvent combined with low alkalinity of the solution, may be caused to deposit the silver in very much finer grains by adding one of a definitely related group of chemical compounds of which thiourea ($\text{CH}_4\text{N}_2\text{S}$) is typical. The proportion of such compound employed is so minute that there is substantial basis for regarding it merely as a catalyzer. However that may be, with a very minute quantity of thiourea, say, 0.3 gram, added to 1,000 grams of the above specified standard developer, or a modification thereof, and in the proper concentration, negatives with an extremely fine grain are reproduced with approximately the same emulsion speed. The important characteristic of the said group of which $\text{CH}_4\text{N}_2\text{S}$ is typical, is that it has generally the following structural composition:



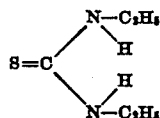
where X is hydrogen, as in thiourea; or any ethyl, allyl, alkyl or aromatic group, which in combination with the nitrogen constitutes an organic radical;

or $\text{N}\equiv\text{C}-\text{S}-\text{X}$ (where X is ammonium, as in ammonium sulfocyanate, or any basic radical).

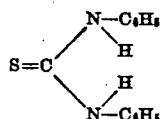
I have discovered no exception to the rule that any such group may be substituted for the hydrogen in the thiourea structural formula, and any resulting compound, which is sufficiently soluble in water, will behave similarly to thiourea. Among those tested are allyl thiourea or thio-sinamine, formula:



Also diethyl-thiourea:

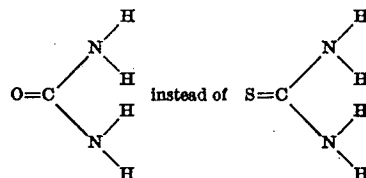


Also, thiocarbamide:

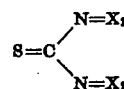


On the other hand, urea has no action on grain

size although it has the same structural form, but has oxygen substituted for sulphur, that is:

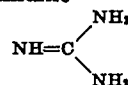


This shows that for fine grain developing, the effective part of the structure of the thiourea and equivalent structures is:



with two hydrogen atoms separately bonded to each nitrogen atom; or with any of the above described equivalent groups bonded to nitrogen in place of one or more of the hydrogen atoms to form therewith a basic organic radical, result in a compound having qualities similar to thiourea. The only theoretical exception to the rule would be where the resulting compound would not be sufficiently soluble in water, or would be attacked and broken down by the concentrated sodium sulphite, or some silver halide developing agent in the solution.

Similarly, as to the ammonium sulfocyanate structure $\text{N}\equiv\text{C}-\text{S}-(\text{NH}_4)$: All sulfocyanates wherein the ammonium is replaced by the radical in the form of an alkaline metal, such as potassium, or sodium; or in the form of an organic alkali, such as guanidine



give a similar grain reducing action, and in this case also the only theoretical exception is where the compound would be one which would be broken down by the concentrated sodium sulphite or some silver halide developing agent in the solution.

While considerable variations in the proportions and even in the kinds of the silver salt reducer, alkali and silver grain solvent, are within the scope of my invention; and while the Eastman developer may be used without change by adding the indicated small proportions of thiourea or equivalent; nevertheless, better results may be attained by certain modifications of the developer, such as slight decrease in the above described Eastman relatively high concentration of sodium sulphite and hydroquinone; together with correlative slight increase of its relatively low alkalinity as determined by the borax or equivalent alkali. As examples, the following may be employed:

Example A

Metal	grams	2
Sodium sulfite	do	80
Hydroquinone	do	4
Borax	do	5
Thiourea	do	0.03
Water	liter	1

Example B

Metal	grams	2
Sodium sulfite	do	80
Hydroquinone	do	4
Borax	do	5
Ammonium sulfocyanate	do	3
Water	liter	1

The proportions of the above may be varied and are approximate. For example, in the relative proportions of the first formula above given, it is possible to change the quantity of thiourea within certain limits; thus I have found that the quantity of thiourea may be .02 gram to .05 gram, and perhaps even wider variations of the thiourea quantity may be made. However, the relative proportion of thiourea is so small that there is substantial basis for regarding it as a catalyzer. Substitution of equivalents is also possible as indicated by the use of ammonium sulfocyanate, which belongs to the same group as thiourea and has analogous properties except, as indicated, the required amount of the ammonium sulfocyanate is approximately 100 times that required for thiourea; also as is well known in the art, about 1/2% of a gram of dry sodium carbonate would produce approximately the same degree of alkalinity as the 5 grams of borax. In the use of each of the above examples, approximately the emulsion speed of the so-called standard developer is obtained, but the silver grains deposited on the negative are greatly reduced as compared with those resulting from the use of said previously known developer. The fact that emulsion speed is not materially reduced is very important because the shadow detail of the pictures is retained without increase in lighting of the subject photographed, and the picture upon the screen is in greater detail than possible through the use of previously known developing compounds, parts of an ensemble not heretofore brought into recognizable projected form on the screen, now clearly appearing through the use of my improved developer.

I am well aware that in attempts to secure fine negative grain, active solvents such as potassium bromide, ammonium iodide and sodium hyposulfite have been proposed to reduce grain size, but their use has been impractical due to the disadvantage of lowering the emulsion speed.

I am also aware that the British Journal of Photography, vol. 59, on pages 840-843 published Nov. 1, 1912, and on pages 860, 861 published Nov. 8, 1912, describes many experiments with developers containing thiourea; but all were for direct development of positive images on the plates, while my invention concerns only development of negatives and only decreasing the size of the silver grains in said negatives. The problems are totally different and involve entirely different ranges of thiourea and alkali concentrations. In the Nov. 1 publication both the thiourea and the alkali are more than a hundred times the maximum usable for fine grain negatives; and in the Nov. 8 publication the least thiourea that would give the positive image was several times, and the maximum something like ten times the maximum usable for developing fine grain of negatives in accordance with the present invention. Moreover the Nov. 8 publication shows that the ranges of thiourea concentration for production of the experimental positives are separated from the ranges required for the present fine grain development of negatives by wide intermediate ranges of failures characterized by "heavy fog", "fogged positive", various "hybrids", etc. This critical intermediate range of inoperative experiment proves a radical difference in kind in the products and in the solutions that produce them. For these and many other reasons, said experiments in no way concern my broad invention; much less do they concern its more specific embodiment in the above described high speed, fine grain mildly

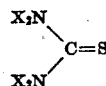
alkaline developers of the conventional balanced type.

It will be evident from the foregoing that the present invention is an improvement limited to, but covering all high speed, fine grain developers for producing negatives, including the above described Eastman D-76 borax developer and all modifications thereof having similar qualities by reason of properly balanced proportions between hydroquinone and metol; and high sodium sulfite concentration as for instance 70 to 100 grams per liter; and alkalinity not less than represented by 2 grams of borax per liter or greater than 15 grams of borax per liter, the maximum amount within said limits, not exceeding that which will result in fogging the negative to an objectionable extent.

For the above and similar high-speed, fine grain developers for negatives, the invention consists in adding an exceedingly small percentage of thiourea or equivalent, specifically not more than .05 gram of thiourea per liter of the solution, and as much less than that as may be necessary to avoid objectionably fogging the negative.

Having described my invention, what I claim and desire to secure by Letters Patent, is as follows:

1. A developer for photographic negatives of the type including a silver halide reducer, 70 grams to 120 grams of sodium sulfite per liter, and an alkaline accelerator having an alkaline effect within the limits producible by 2 grams to 15 grams of borax per liter, all in quantities and proportions conventionally balanced for development of fine grain negatives and containing a reagent of the following structural composition:



where X is selected from the group consisting of hydrogen and allyl, alkyl, and aryl radicals; said selected reagent being in quantity affording a grain reducing effect equivalent to that of 0.01 to 0.05 gram of thiourea per liter of the developing solution.

2. A photographic developer of the type conventionally balanced for development of fine grain negatives and containing substantially the following constituents in approximately the following proportions: metol 2 grams, sodium sulfite 70 grams to 120 grams, hydroquinone 4 grams, borax 5 grams, thiourea 0.03 gram, and water 1 liter.

3. A photographic developer of the type conventionally balanced for development of fine grain negatives and containing substantially the following constituents in approximately the following proportions: metol, 2 grams; sodium sulfite, 70 grams to 120 grams; hydroquinone, 4 grams; borax, 5 grams; together with 0.01 to 0.04 gram of thiourea per liter of the developing solution.

4. A photographic developer of the type including a silver halide developing agent, 70 grams to 120 grams of sodium sulfite per liter and an accelerator affording alkalinity equivalent to 2 grams to 15 grams of borax, all in quantities and proportions conventionally balanced for development of fine grain negatives from high speed plates or films, together with 0.01 gram to 0.04 gram of thiourea per liter of the developing solution.

5. A solution for developing high speed silver halide emulsion plates or films to produce photo-

graphic negatives, said solution containing 70 to 120 grams of sodium sulfite per liter, a reducing agent for the silver halide grains of the negative image, an alkaline agent consisting of approximately 2 grams to 10 grams of borax per liter of the solution, and containing also about .01 gram to .04 gram per liter of thiourea.

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6. A fine grain developer for producing nega-

tives from high speed emulsions, including per liter of water about 2 grams of metol; between 70 and 120 grams of sodium sulphite, an alkali having an alkalizing effect equivalent to 1 to 5 grams of borax per liter; and 0.01 to 0.05 gram of thiourea.

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