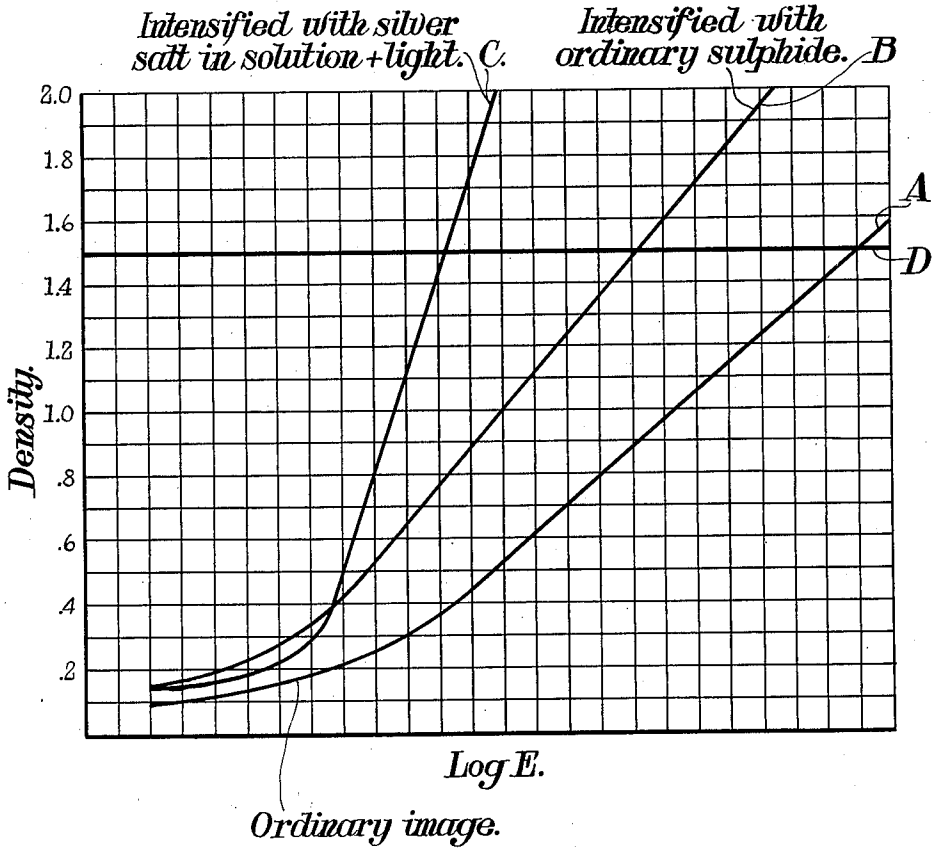
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PROCESS AND SOLUTION FOR TREATING PHOTOGRAPHIC IMAGES

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PROCESS AND SOLUTION FOR TREATING PHOTOGRAPHIC IMAGES

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9 Claims. (Cl. 95—88)

This invention relates to processes for treating photographic images and photographic intensifying solutions useful therein, and particularly to solutions for intensifying silver sulphide images and images containing other insoluble salts of silver. The invention contemplates the use of light to accelerate the action of the solutions on the images, although in certain cases the action can be made to proceed slowly in the dark.

The complete process comprises two main parts: first, the transformation of a silver image into a silver compound image and second, the intensification of the silver compound image. Many processes for the first part have heretofore been known, particularly when the silver compound image is one of silver sulphide, but it is our belief that the second part is altogether new. However, the final image is profoundly affected by the particular methods used in the first part and by the character of the sulphide image before intensification. We have found certain methods of sulphiding to be particularly desirable, particularly those of the two-step type in which the silver image is first bleached and then sulphided. Our complete preferred process consists therefore of three steps; first, bleaching a silver image; second, transforming the bleached image into silver sulphide (the above two steps constituting the first part of the process) and, third, intensifying the sulphide image; this third step constituting the second part of the process and containing in itself a high degree of novelty, particularly in that embodiment which includes the action of light.

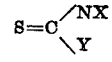
It has long been known that solutions of silver halides in sodium thiosulphate will deposit silver sulphide very slowly. This deposition, we found, could be accelerated by using dilute solutions relatively rich in silver and poor in thiosulphate. The solutions are most active when the silver is present in greater concentration than could be secured by dissolving the silver halides in hypo. In investigating this further, we have evolved a novel intensifying method and intensifying solutions of a new kind having new properties.

The solutions which form the chief part of the present invention have the property of intensifying deposits of silver sulphide and leaving substantially unchanged deposits of metallic silver. Indeed, a silver sulphide deposit may be distinguished from a silver deposit by its behaviour in these solutions. Accordingly photographic silver images may be converted to silver sulphide in any of the well known ways and may then be intensified by submitting them to the action of one of the solutions described below, preferably in the presence of light.

Reference will be made to the accompanying drawing the single figure of whch is a chart presenting curves showing results which may be secured with our invention.

The solutions which we have found may be used to intensify silver sulphide deposits contain a silver salt which is itself a mild reducing agent, or is accompanied by a separate mild reducing agent. Thus we find that solutions of silver sulfide in an excess of sodium sulphite, together with a small proportion of bisulphite, are powerful intensifiers for a silver sulphide image when the latter is immersed in the solution under quite moderate illumination from daylight or from an ordinary tungsten lamp. It should be noted that the sulphite radicle in the solution is here serving as the mild reducing agent. Solutions of silver citrate and other silver salts in sodium sulphite solution are effective. Aqueous silver sulphate containing a little hydrazine sulphate or hydroquinone or pyrogallic acid exhibits intensifying properties. Ammoniacal silver nitrate containing a soluble sulphite is effective. An example of a silver salt capable of functioning without a reducer is silver nitrite dissolved in ammonium hydroxide. Alternatively, the silver nitrite may be dissolved in an excess of sodium nitrite solution. Silver nitrite intensifies a sulphide image very rapidly.

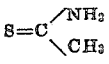
The above mentioned solutions are much more effective in the presence of light than in the dark. There is, however, a second class of solutions which, in addition to a soluble silver salt, contain compounds providing labile or nascent sulphur. They intensify excellently in the dark, and may be only slightly accelerated by light. These solutions comprise a soluble silver complex such as the sodium silver sulphite or sodium silver thiosulphate, together with a sulphiding body which may be inorganic or organic. Solutions containing the soluble sodium silver sulphite complex, together with one or more of such compounds as the alkali thiosulphates, hydrosulphites, tri-, tetra- and penta-thionates; unsaturated organic bodies of the grouping



and, indeed, any of those sulphur-bearing bodies which are described as photosensitizers in the U. S. patent of S. E. Sheppard, No. 1,574,944, issued March 2, 1926, and as activators for plat-

ing solutions, in our Patent No. 1,857,507, issued May 10, 1932, afford workable intensifiers.

While most bodies containing available sulphur can be used to compound sulphide intensifiers, not all are desirable, owing to their odor, volatility, insolubility, and other objectionable properties. The organic sulphide type of intensifier may be exemplified by the use of thioacetamide



In this class of intensifier the balance between the silver complex and the sulphiding agent is adjusted so delicately that the silver sulphide tending to deposit from the solution does so only where there is already a deposit of silver sulphide. A poorly compounded intensifier fails to deposit at all, or else deposits both in the image and in the clear portion of the photograph.

The intensifying reaction occurs between the soluble silver in the solution and the very insoluble silver sulphide image. The greater the surface area or dispersity of this image, the quicker and more abundant is the intensification. The many methods of toning in common use (for instance, see British Journal Almanac 1932, page 369) aim at converting the silver image to sulphide with the least disturbance of the individual grains, since such a procedure yields the preferred colder tones. While images sulphided in the conventional way intensify excellently, images in which the grain has been purposely disrupted show an enhanced effect. The usual two-stage conversion of the original silver, which comprises bleaching and sulphiding, offers two opportunities of disruption.

According to the preferred form of our invention, we disperse the image during bleaching by using a powerfully oxidizing solution relatively poor in silver precipitant.

Formula No. 1 (Bleach)

	Parts
Potassium permanganate	1
Potassium bromide	1
Sodium acetate	2
Acetic acid	2
Water	100

The image is rinsed and may be cleared in

	Parts
Sodium bulsulphite	1
Water	100

After a short wash, the bleached image may be darkened or sulphided in a solution of sodium sulphide containing a silver bromide solvent such as, for instance, sodium thiosulphate, ammonium hydroxide or ammonium thiocyanate. A useful darkening bath is made from:

Formula No. 2 (Sulphiding solution)

	Parts
Sodium sulphide	1
Sodium thiosulphate	5
Water	100

The image is now washed thoroughly and may then be dried before transferring to the intensifying solution, or it may be transferred direct.

Either of the two types of intensifiers already mentioned may be used. Two examples of the first type, useful in the presence of light, in the manner already described are as follows:

Formula No. 3 (Intensifier)

	Parts
Silver nitrate	1
Sodium sulphite	5
Sodium bisulphite	2
Water	100

or

Formula No. 4 (Intensifier)

	Parts
Silver nitrate	0.6
Water (about)	50

Sodium nitrate 10% solution, quantity sufficient to redissolve precipitate first formed, then add water to make, 100 parts.

As examples of the second type of intensifiers, which can be used in the absence of light, the following are given:

Formula No. 5 (Intensifier)

	Parts
Silver sulphite	1
Sodium sulphite	4
Sodium bisulphite	1.6
Water	20

After the solution of these ingredients, there are added 1.5 parts of sodium thiosulphate and the solution is then diluted to 1000 parts with water.

To intensify, the silver sulphide image is allowed to remain in this completed solution for periods which may vary from 1 to 24 hours, depending on the quality of the original image and the result desired.

Another intensifier of the second type and embodying an organic sulphiding agent follows:

Formula No. 6 (Intensifier)

	Parts
Silver nitrate	1
Sodium sulphite	4
Potassium bisulphite	1½
Thioacetamide	.3
Water	100

The sulphide image is immersed in the solution, and sodium acetate (10% solution) is added until the intensifying action begins.

There are certain novel and useful features associated especially with the first type, the light-activated or "optical" intensifiers, which are seldom found in other intensifying solutions.

The intensification is very great. Intensification embodying a chemical reaction where an exact equivalent of some secondary pigment is added to the image, as, for instance, in the well known mercury ammonia intensifier, where the total change is

$$Ag \longrightarrow AgHgCl.NH_2$$

can only cause a limited increase in density. Physical intensifiers, where the image serves as a nucleating agent for additional deposit which is nascent in solution, can give a more powerful intensification only limited by the tendency to stain.

Optical intensifiers compounded according to our invention combine the non-staining properties of a chemical intensifier with the vigor and control of a physical intensifier. Light turns the solution into a physical intensifier only where the image is situated.

An allied feature possessed by optical intensifiers of the kind described is the control of minimal intensification which is possible to varying the bleaching and sulphiding conditions. With certain sulphiding mixtures, notably those richer

in silver halide solvent, the intensification only begins after a certain minimum density of image. Thus, an image sulphided in

Formula No. 7 (Sulphiding)

	Parts
Sodium sulphide	1
Ammonium hydroxide (standard solution)	2
Water	1000

may show no intensification of original densities from 0.00 to 0.05. At an original density of .06 intensification begins, converting the .06 to .18, for example, and for an original density of .1 onwards all the densities may be multiplied by 12, an original .3 becoming 3.7 in a particular experiment.

When, for sulphiding the bleached image, the following solution is used:

Formula No. 8 (Sulphiding)

	Parts
Sodium sulphide	2
Potassium thiocyanate	1
Ammonia (conc.)	3

intensification is negligible for densities below .1, but is equally vigorous for all densities above this point in the scale.

These solutions, and the corresponding density values, are given only by way of example, and there is much variation in the finished tone scale according to the nature of the original sensitive material. It is, however, a general property of solutions compounded and used according to our invention that they intensify the significant portions of the tonal scale, and neglect the lower fog densities. The degree of this neglect can be enhanced by the presence of a suitable silver halide solvent in the sulphiding bath, as in Formulæ 2, 7 and 8.

While our invention concerns mainly silver sulphide images immersed in silver-bearing solutions in the presence of light, it is intended to include other silver compound images treated in the same manner. Thus, images composed of silver sulphide, selenide, telluride, thiocyanate, azide, bromide, chloride, or iodide all intensify when placed in a solution such as the following:

Formula No. 9 (Intensifier)

	Parts
Silver nitrate	1
Sodium sulphite	5
Sodium bisulphite	1½
Water	100

and exposed therein to the action of light. The degree of intensification is determined, other things being equal, by the time of exposure and the intensity of the light. The colorless silver images intensify more readily in blue light while the colored images, such as sulphide, selenide, and telluride, are also markedly sensitive to the red and infra-red.

The insoluble salts other than silver sulphide, described as capable of intensification, are all simple binary compounds of silver with another radicle, thus AgX^- or $Ag_2X^=$ or $Ag_3X^{\equiv}$, etc. (such, for instance, as silver phosphate Ag_3PO_4). It is not expected that the heavy, colored, very complex deposits obtained by such toning processes as the well known copper ferrocyanide or iron ferricyanide processes, which leave some silver in the resulting images, will afford a suitable base for further optical intensification.

A satisfactory intensifier which contains silver nitrite may be made as follows:

Formula No. 10 (Intensifier)

To a 1% solution of silver nitrate is added a solution of sodium nitrite until the precipitate formed is redissolved.

This solution is then used, along with the action of light, to intensify silver compound images as previously described.

Although the examples hitherto given all describe silver metal depositing on silver sulphide from a silver-bearing solution, we have found that in certain cases other metals may be substituted. Thus, in the type of bath where intensification occurs spontaneously in the dark, copper salts and the salts of other metals yielding colored sulphides may be substituted for silver with varying success. We may therefore use other metallic salts which produce a like or allied effect.

We will now describe certain novel uses to which our intensifying solutions may be put: The ability of these solutions to give great intensification action on small and moderate densities, while at the same time neglecting the very smallest or fog densities, enables them to be used for improving the shape of the toe of the characteristic H & D curve on many materials. We are, for example, able to intensify faint deposits so that the toe of the curve is apparently partially smoothed out and made a prolongation of the straight-line portion. This property is illustrated in the drawing, which shows H & D curves of a common photographic material. Curve A represents the original normal image; Curve B, the image intensified in a solution (Formula No. 3) after sulphiding in a plain sodium sulphide solution; Curve C, the image obtained by intensification in a solution containing a silver salt after sulphiding in the presence of a silver solvent as described.

It is well understood that two methods are in vogue for estimating the speed of a photographic material. In one case the speed is judged by the nearness to the density axis at which an extension of the straight-line portion of the characteristic curve cuts the log E axis. Defined in this manner, intensification according to our invention does not necessarily increase the speed. However, the speed of a material may be defined, for certain purposes, in terms of the minimum exposure needed to produce a given density (for instance, D=1.5). Judged according to this standard, the intensification process produces a very great increase in speed indeed. Thus, in the figure, an original density of .3 is intensified to a density of 1.7 producing an apparent increase in speed of nearly 6 times. In actual practice, we find a speed increase of 10 or 12 times not uncommon. The practical application of such a speed increase can readily be seen. Sound track images too faint for reproduction in talking picture apparatus may be increased in density until they give faithful sound reproduction. In a similar manner, astronomical and spectrographic images may be increased from poor visibility to useful and measurable densities.

The method we have described, as will be seen, is carried out very conveniently on any normal type of positive or negative photographic material in which the image may be converted into one of silver sulphide.

In the solutions of the type described many variations are possible. They are given only by way of example and the proportions given are not critical. We consider as included in our invention

all modifications and equivalents coming within the scope of the appended claims.

What we claim is:

1. In a process of intensifying a silver compound image, the step which comprises submitting it to a bath containing initially a silver salt, and an alkali bisulphite and an alkali sulphite.

2. In a process of intensifying a silver sulphide image, the step which comprises submitting it simultaneously to the action of light and of a bath containing as an initial ingredient, a silver sulphite, an alkali bisulphite and an alkali sulphite.

3. In the process of intensifying a silver compound image, the step which comprises submitting it simultaneously to the action of light and of a bath containing silver nitrite dissolved in an alkali nitrite.

4. In the process of intensifying a silver sulphide image, the step which comprises submitting it simultaneously to the action of light and of a bath containing silver nitrite dissolved in an alkali nitrite.

5. In the process of intensifying a silver sulphide image, the step which comprises submitting it to the action of a bath containing a silver salt, sodium sulphite and sodium bisulphite, and sodium thiosulphate.

6. The process of intensifying a photographic silver image which comprises bleaching said silver image in a solution containing an oxidizing agent and relatively poor in silver precipitant, darkening the bleached image in a solution containing sodium sulphide and a solvent for silver bromide, and then intensifying the resulting silver sulphide image in a solution containing sodium sulphite and a silver salt.

7. The process of intensifying a photographic silver image which comprises bleaching said silver image in a solution containing an oxidizing agent relatively poor in silver precipitant, darkening the bleached image in a solution containing sodium sulphide and a solvent for silver bromide, and then intensifying the resulting silver sulphide image in a solution containing sodium sulphite, sodium bisulphite, sodium thiosulphate and a silver salt.

8. The process of intensifying a photographic silver image which comprises bleaching said image in a solution containing an oxidizing agent and relatively poor in silver precipitant, bathing the bleached image in a solution containing sodium sulphide and a solvent for silver bromide whereby a fine grained silver sulphide image is formed, and then submitting the image to a bath containing in solution a silver salt and a mild reducing agent whereby the image is intensified.

9. The process of intensifying a photographic silver image which comprises bleaching said image in a solution containing an oxidizing agent and relatively poor in silver precipitant, bathing the bleached image in a solution containing sodium sulphide and a solvent for silver bromide whereby a fine grained silver sulphide image is formed, and then submitting the image in the presence of light to a bath containing in solution a silver salt and a mild reducing agent whereby the image is intensified.

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