Dec. 5, 1967 KINTARO NASU ETAL 3,356,502

AMMONIUM OR ALKALI METAL THIOCYANATE AQUEOUS RINSE SOLUTION FOR STABILIZED SILVER PHOTOGRAPHIC IMAGES

Filed May 28, 1965

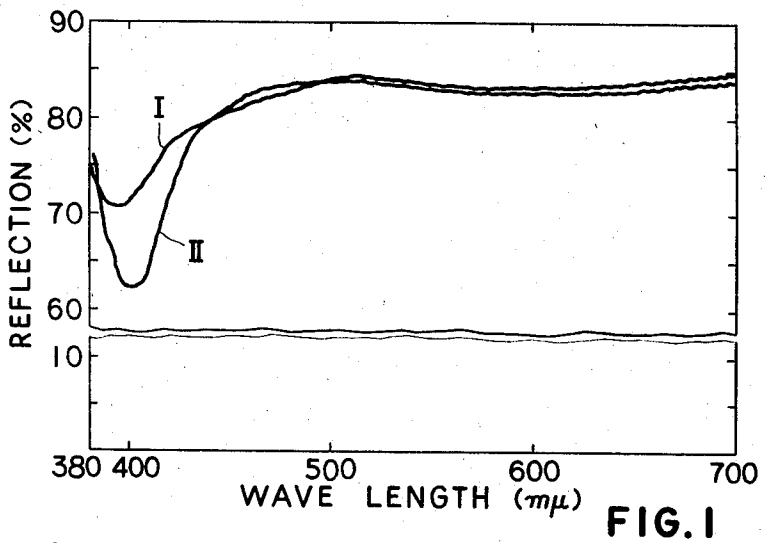

FIG. 1

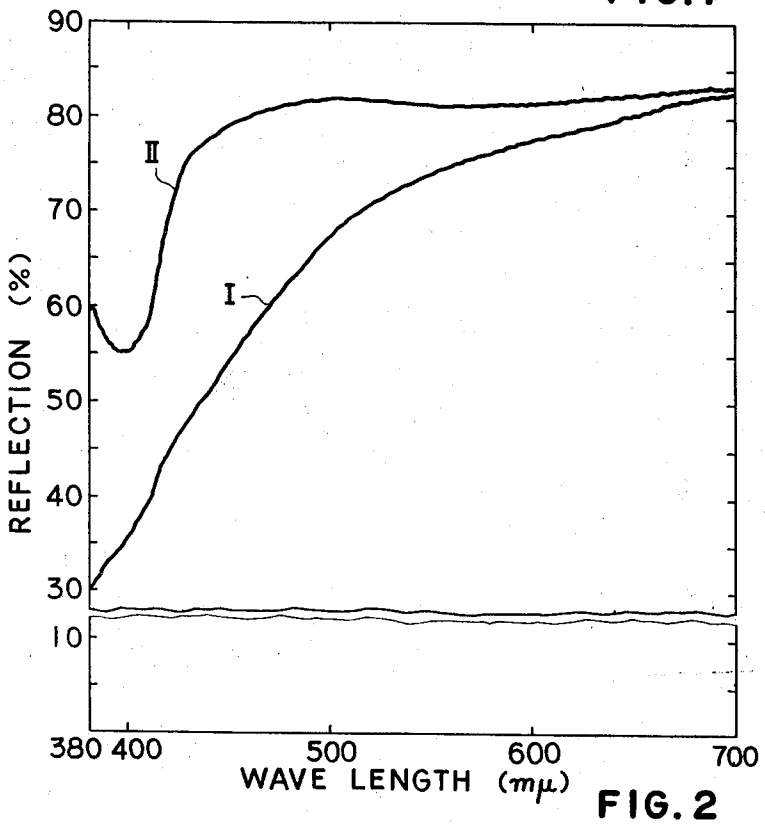

FIG. 2

INVENTORS
KINTARO NASU
TATSUYA TAJIMA
BY TAKAO KANA
Buckman and Archer
THEIR ATTORNEYS

United States Patent Office 3,356,502 Patented Dec. 5, 1967

3,356,502

AMMONIUM OR ALKALI METAL THIOCYANATE AQUEOUS RINSE SOLUTION FOR STABILIZED SILVER PHOTOGRAPHIC IMAGES

Kintaro Nasu, Tatsuya Tajima, and Takao Kano, Kanagawa-ken, Japan, assignors to Fuji Shashin Film Kabushiki Kaisha, Kanagawa-ken, Japan, a corporation of Japan

Filed May 28, 1965, Ser. No. 459,802
Claims priority, application Japan, June 25, 1964, 39/35,748
1 Claim. (Cl. 96—50)

This invention relates to an improved silver halide photographic method. More particularly, the invention relates to a process for the rapid treatment of a photographic material to give improved printed images.

A rapid treatment system for photographic materials to form silver images without the necessity of a so-called "fixing and rinsing treatment" has been already known. In such a system, a photographic print is, after being developed by a conventional method, treated with a solution of a stabilizing agent, such as ammonium thiocyanate, and is dried immediately without being rinsed. In this treatment, a fixing procedure is unnecessary and therefore the period of time for treating light-exposed photographic materials can be reduced. Such various rapid treatments for photographic materials are described in, e.g., H. D. Russell, B. C. Yackel and G. S. Bruce; Photographic Science and Technical Journal; August, pp. 59–62 (1950), Broughton et al., U.S. Patent 2,614,927 (published on Oct. 21, 1952), and Brice, U.S. Patent 2,448,857 (published on Sept. 7, 1948).

The stabilizing agent used generally in such rapid treating processes is a compound having a double-bonded sulfur or an —SH linkage, for example, alkali metal thiocyanate, ammonium thiocyanate, an alkali thiosulfate, ammonium thiosulfate, thiourea, and thioglycol. The stabilizing treatment using such a stabilizing agent makes the rapid treatment possible but is accompanied with many defects in the treated prints. For example, since the above-mentioned stabilizing agent is used in an amount considerably larger than the theoretical amount necessary to secure the light-stability of thus stabilized print and since the stabilizing agent is hygroscopic, complete drying of the print is difficult and the surface of the print is sticky. Moreover, since the stabilizing agent gradually oxidizes metallic silver of the images in the print into a silver complex salt, the image density is reduced or vanished, and the color tone of the image is changed from black to brown or yellow. Such a fading phenomenon is liable to occur in particular when the print is stored under high humidity. Further, if a photosensitive material is exposed to light when the reaction between the undeveloped silver halide and the stabilizing agent is not finished, photo-decomposition of the non-stabilized silver halide occurs, which stains the white portions and transparent portions of the treated photosensitive material.

Therefore, an object of this invention is to provide a process for improving the quality of prints by removing the above-mentioned general defects in the rapid treatment system. Namely, the first object of this invention is to reduce the hygroscopicity of the print and to remove the stickiness of the surface of the print. Further, the second object of this invention is to reduce the density of salts in the treated photosensitive layer of the print and to enable "ferrotype finishing." While "ferrotype finishing," i.e., a treatment for smoothing the surface of the print by pressing the print into contact with a heated metal plate, can not be applied in conventional stabilizing treatments, or, if it is possible, the ferrotyped print loses gradually its luster, it can be adopted suitably and

effectively in the process of the present invention. Still further, the third object of this invention is to improve the whiteness of the white portions and the transparency of the transparent portions of the treated print and to prevent discoloring of the treated print into yellow or orange caused by exposing it to a light which contains a light near the ultraviolet range, e.g., to sunlight.

These objects can be achieved by the process of this invention, by treating a photographic layer stabilized with ammonium thiocyanate and/or an alkali metal thiocyanate for a short period of time, preferably, for 1–10 minutes with a solution containing same or different thiocyanate compounds in a concentration of 1–15 percent by weight, that is, a concentration lower than that of the solution containing the thiocyanate compound or compounds used for the stabilization. If the concentration of the solution is lower than 1%, the thiocyanate or thiocyanates in the photographic layer flow out of the layer, which makes the stabilization insufficient. On the other hand, if the concentration is above 15%, the amount of the thiocyanates in the photographic layer is increased to an amount more than is necessary and the metallic silver of the image in the print is easily attacked by the compounds.

Hitherto, it was an object of the rapid treatment to finish the development and the stabilization within at least 1 minute, and usually in a short period less than 10 seconds. Hence, the concentration of the stabilizing agent was increased as high as possible. But almost all of the practical stabilizing agents have extremely high solubilities, and while the stabilization rate was high, the density of salts in the photographic layer of the print was also high, resulting in increasing the hygroscopicity and stickiness of the layer as well as in causing fading of the images.

As countermeasures, there have already been known the addition of a noble metal salt and an organo-mercapto compound, the use of a thiosulfate together with the thiocyanate (E. T. Smith and G. W. W. Stevens; U.S. Patent 3,132,943, published on May 12, 1964), and the addition of a sulfite, bisulfite or metabisulfite of an alkali metal or ammonium. However, while fading of the silver image and discoloring of the white portions and transparent portions may be prevented by such treatments, the effect is not complete and the stickiness of the surface of the emulsion layer of the print is usually hardly reduced.

By the process of the present invention, the stickiness of the surface layer of the print is almost completely removed and has the same surface properties as that of a print subjected to fixing and rinsing treatments. This enables the print to be subjected to "ferrotype finishing," and, after ferrotype finishing, the print treated by the process of this invention can keep its luster for a long period of time. Further, by adding a fluorescent whitening agent or a noble metal salt, organo-mercapto compound or thiosulfate shown in the above-mentioned patents into the second stabilizing bath of this invention, the fading of the silver image and the whitness can be further improved.

The stabilization process of this invention is conducted substantially in two stabilizing baths, but if only the period of time for the first stabilization is prolonged, the print can be stabilized and the similar effect as that of this invention can be obtained by only the first stabilizing bath. That is, by prolonging the treating period, the effects for enabling the application of ferrotype finishing and preventing yellowing of the print by ultraviolet rays can be obtained. However, in the latter case, the stabilization period is prolonged in vain when the effects by the process of this invention are not desired, which is undesirable in a point of a so-called rapid treatment, and

by carrying out the stabilizing treatment in a two-bath system as in the case of this invention, an adaptable treating system can be obtained with or without applying ferrotype finishing (to the surface or the backside surface) according to purposes to be required. Of course, the use of a suitable diluted one-solution stabilizing system may be regarded as an embodiment of this invention.

Further understanding of the novel process of this invention can be obtained from the following examples, which disclose the preferred modes of this invention.

Example 1

A gelatin-silver chloride emulsion containing hydroquinone was applied on a baryta paper to form a photosensitive paper, which was then, after being exposed and developed, treated by a stabilizing solution having the following composition;

Water (50° C.)	ml	500
Ammonium thiocyanate	g	250
Sodium bisulfite	g	70
Sulfuric acid monomethyl-p-aminophenol	g	2
1-phenyl-5-thiol tetrasol (1% alcohol solution)	ml	60
$CoSO_4$	g	0.3

Water to make 1 liter.

When the treatment was carried out at room temperature, the development and the stabilization treatment was finished sufficiently in about 10 seconds. As the stabilized print was obtained in a semi-dried state, the surface of the print lacked the luster of a ferrotype-finished print, although the treated print could be considered sufficiently satisfactory.

The thus treated print was immersed for about 3 minutes in an aqueous solution (the second stabilizing bath) prepared by diluting the first stabilizing solution with water to 6 times its original volume, the excess solution was lightly wiped away, and the print was processed on a ferrotype machine. A finished print was obtained which was by no means inferior to a print subjected to fixing, rinsing and ferrotype finishing. Thus, the second stabilizing bath greatly improved the quality of the print subjected to only one stabilizing bath.

The results of measuring the luster of the print subjected to the second stabilizing treatment and the print subjected to the usual one-bath stabilizing treatment are shown in the following table. The measurement was made by using a luster meter with the angle of incidence 60°.

	Directly after ferrotype finishing	After 2 weeks from ferrotype finishing
Treated by only the 1st stabilizing bath	65	59
Immersed in the 2nd stabilizing bath after the 1st stabilizing treatment	100	98

The use of a second stabilizing bath not only results in a print of higher luster after ferrotype-finishing, but also significantly decreases the loss in luster occurring after storage at room temperature and normal humidity, as compared to the use of the usual single-bath stabilization.

Example 2

After treating the same silver chloride photosensitive paper as in Example 1 with the same stabilizing solution (1st stabilizing bath) as in Example 1, the photosensitive layer was immersed for 5 minutes in an aqueous solution (2nd stabilizing solution) of 3.5 weight percent of ammonium thiocyanate and subjected to ferrotype finishing. The thus obtained print had similar features to the print obtained through the use of the second stabilizing bath in Example 1.

Example 3

When the procedure of Example 1 was used with an aqueous solution of 4 weight percent of potassium thiocyanate as the second stabilizing bath, a print having the same features as in the case of Example 1 was obtained.

Example 4

A photosensitive paper prepared by applying on a baryta paper a gelatin-silver bromide emulsion containing a small amount of the bromide was light-exposed and developed by a surface coating process with a developing solution having the following composition:

	G.
Sodium hydroxide	22.5
Sodium sulfiate (anhydrous)	80
Hydroquinone	36
Potassium bromide	0.5
Pyrazone	2

Water to make 1 liter.

The developed photosensitive paper was then treated with a stabilizing solution (1st stabilizing bath) having the following composition:

Potassium thiocyanate	g	300
Potassium metabisulfite	g	50
Sodium sulfite (anhydrous)	g	15
Glacial acetic acid	cc	40
Sodium phosphate (Na_2HPO_4)	g	15

Water to make 1 liter.

The first stabilizing treatment was carried out as in Example 1, the thus treated sensitive paper was immersed in a second stabilizing bath containing 4 weight percent of ammonium thiocyanate and 0.1 weight percent of a fluorescent whitening agent such as Whitex 3B (trade name by the Sumitomo Chemical Industry Co.) for 3 minutes and then was subjected to ferrotype finishing. By this treatment, a print having the features as in Example 1, as well as having extremely good whiteness and a sharp image contrast, was obtained.

In order to clarify the effect of the process of this invention, spectral reflectivity curves of a print (II) prepared with the second stabilization treatment of this invention and a comparative print (I) prepared with no second stabilization treatment are shown in the accompanying drawings. As shown in FIG. 1, there are no large differences between the print (II) and the comparative print (I) directly after ferrotype finishing, but as shown in FIG. 2, the reduction (yellowing) of the whiteness of the print (II) when exposed to daylight for about 24 hours is substantially less than that of the print (I). Since the whitening effect of a fluorescent whitening agent does not show up in the curves, the practical whiteness of the print (II) is better than that shown in the figures.

Example 5

The composition of the second stabilizing bath in Example 4 is replaced with 5 weight percent of potassium thiocyanate and 0.5 weight percent of Whitex 3B. By using the above stabilizing bath, the same effect as in Example 4 was obtained with an immersion period of 1 minute. Further, the deterioration of the second stabilizing bath caused by treating many prints was less than in the case of the second bath of Example 4.

Example 6

By replacing the composition of the second stabilizing bath in Example 4 with 4 weight percent of amonium thiocyanate and 6 weight percent of potassium metabisulfite, almost the same results as in Examiple 4 were obtained with an immersion period of 5 minutes. In this case, a fluorescent whitening effect could not be obtained but other properties of the obtained print were almost the same as those in Example 4.

Example 7

In the case of a low-luster paper, such as where the surface of the photosensitive paper in Examples 1–6 was

matted or semi-matted, and in the case of a paper having a specific surface property, such as a silk surface or a fine-grained surface, the first and the second stabilization treatments were carried out as in the above examples except that ferrotype finishing was applied to the back side of the paper. By these treatments, a print having reduced yellowing by daylight and a reduced surface stickiness was obtained.

We claim:

In a process for the rapid treatment of a silver halide photographic material wherein the silver halide photographic material is developed, the developed material is stabilized with a stabilizing bath containing at least one compound selected from the group consisting of ammonium thiocyanate and an alkali metal thiocyanate, and is then dried, the improvement which comprises immersing the developed material, after the stabilizing bath and before the drying, in an aqueous solution containing at least one of said compounds in a concentration of 1 to 15 weight percent and less than the concentration of said stabilizing bath.

References Cited

UNITED STATES PATENTS

2,614,927 10/1952 Broughton et al. ------- 96—61

OTHER REFERENCES

John, D. H. O., et al.: Photographic Chemistry, New York, Reinhold Publishing Corporation, 1963, page 157.

NORMAN G. TORCHIN, *Primary Examiner.*

C. E. DAVIS, *Assistant Examiner.*