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3,093,479

**USE OF QUATERNARY AMMONIUM COMPOUNDS
FOR STABILIZING PROCESSED PHOTOGRAPHIC
ELEMENTS**

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This invention relates to processes for stabilizing processed photographic elements against sulfiding, image fading, and staining, and for preventing the growth of fungi, thereon.

In the processing of photographic developing-out materials such as gelatino-silver halide emulsions coated on paper, film, or glass supports, if, after fixation, the hypo (usually sodium or ammonium thiosulfate) is not completely eliminated from the processed material by washing or other means, the silver image will tend to "fade" or change color under usual conditions of temperature and humidity during storage.

This fading is a result of the conversion of more or less of the silver image to silver sulfide by the sulfur present in the residual hypo. This is manifest by a change in hue of the image first to yellowish brown, then to yellow, and in most cases the change is accompanied by a yellowing of the unexposed portions of the image. This yellowing of the highlights is a result either of the use of an exhausted fixing bath, or insufficient fixation and washing, resulting in the retention of complex silver-sodium thiosulfates which under proper conditions decompose to give a yellow silver sulfide.

In addition to attack of the silver image by the sulfur bearing decomposition products of hypo within the gelatin layer, many external agents also attack the silver image, the most significant being hydrogen sulfide which is present in coal gas (illuminating gas). High humidity and temperature accelerate this reaction tremendously. Sulfur dioxide and other acid gases in the presence of the hypo in the image layer also accelerate the "fading" of the image.

The rate at which a silver image fades depends upon many factors including (1) the concentration of hypo in the image layer, (2) the concentration of hydrogen sulfide and other gases in the atmosphere, (3) the grain size of the silver image and (4) the temperature and humidity of storage. Thus, a content of residual hypo as low as 0.005 milligram per square inch may cause fading with fine-grained images, especially in the case of photographic paper prints. Similarly, the combination of high humidity and high temperature which usually exists in tropical countries is fatal to a photographic print containing hypo.

The prevention of yellowing or fading of black-and-white prints or films usually required the use heretofore of multiple fixing baths and prolonged washing, or the use of a complex oxidizing bath to chemically alter retained thiosulfate compounds to forms which were readily removable or which could not produce fading or yellowing. Oxidizing agents such as the hypochlorites, iodine, potassium permanganate, and hydrogen peroxide are all well known in photography but there are disadvantages in using each of them. For example, hypochlorites or potassium permanganate attack the images of fine grain materials, such as prints and fine grain films, when they are used in sufficient concentrations and acidities to rapidly oxidize hypo. The same is true of iodine and, to a lesser extent, of hydrogen peroxide (in the absence of alkali) since they oxidize hypo principally to tetrathionate which, like hypo, can act as an agent in promoting image fading.

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In addition to the problem of fading, photographic elements, especially those containing gelatin, are quite subject to attack by fungus organisms when stored for periods of time under conditions of high temperature and humidity such as is common in tropical climates. Usually such fungus growths are very destructive to photographic prints or films.

It is, therefore, an object of the present invention to provide a new method for treating processed photographic elements which will effectively stabilize the photographic image against sulfiding and the resulting image fading and staining even when the elements contain appreciable residual sodium thiosulfate and/or silver thiosulfate complex. A further object is to provide a method for stabilizing processed photographic elements which contain sodium thiosulfate and/or silver thiosulfate complex so that they do not fade or become stained during storage in tropical conditions. A further object is to provide a method for stabilizing processed photographic elements containing thiosulfate compounds without, at the same time, forming other compounds such as tetrathionate that also promote image fading. A further object is to provide a method of stabilizing processed photographic elements containing thiosulfate or a silver complex without using unstable oxidizing agents such as hydrogen peroxide. A still further object is to provide treatment for processed photographic elements which not only stabilizes the photographic image against fading and staining, but which also prevents the growth of fungus on the photographic element even when stored under tropical conditions. Other objects will be apparent from the description and claims which follow.

These and other objects are accomplished by means of this invention as described hereinafter. We have discovered a simple, rapid chemical treatment that effectively protects processed photographic elements against chemical and microbiological deterioration. The process embodying the invention is effected by treating a developed and fixed photographic element in an aqueous solution of a quaternary ammonium salt as defined herein, and then drying it without further washing.

The process is characterized by using small quantities of chemicals which are nonvolatile, chemically stable, cheap, readily available, readily soluble in aqueous solution, colorless, safe to handle, and nontoxic to human beings. It does not require the use of multiple fixing baths, prolonged washing or the use of unstable chemicals such as hydrogen peroxide or the use of toxic chemicals such as iodine, potassium permanganate, etc. The process does not require that the fixing bath be fresh in order to prevent subsequent chemical deterioration of the photographic images produced. Exhausted fixing baths containing as much as 3 g. of silver per liter are used with excellent results in our process. Furthermore, the fix bath wash may be shortened from that required in other processes since it is not necessary in our process to remove all of the thiosulfate compounds from the photographic material. In fact, it is actually desirable to have residual thiosulfate compounds in the image layer in order to get optimum stabilization of the photographic image.

Our process stabilizes the photographic element so that sulfiding with the resulting yellowing and image fading will not occur even after long periods of storage at the undesirably high temperatures and humidities normally found in the tropics. This protection is very effective against sulfiding that would normally occur from the decomposition of residual thiosulfate compounds in the image layer and also from the effect of exterior sulfiding agents which come into contact with the photographic element during long periods of storage. Not only is the treatment of our invention effective

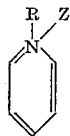
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as a stabilizer against chemical deterioration but it also protects the treated prints or film against the attack of fungus and other microorganisms that are found in the temperature zones but are especially active and destructive in the tropics.

The quaternary ammonium salts which are used in the anti-sulfiding and fungicidal treatment embodying our invention are surface active agents having the formula:

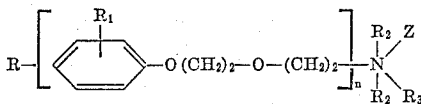


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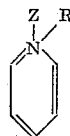


wherein R, R₁, R₂, and R₃ may be alkyl, aryloxyalkoxy-alkyl, aryl, arylalkyl radicals in which there are usually 1 to 20 carbon atoms, and Z is a halogen atom or other anion such as sulfate or an acetate radical.

The quaternary ammonium salts which are usually employed have the formula:

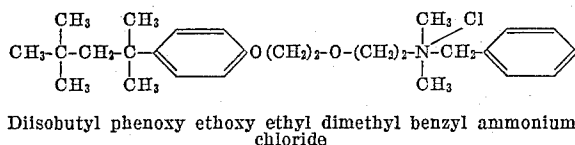


or

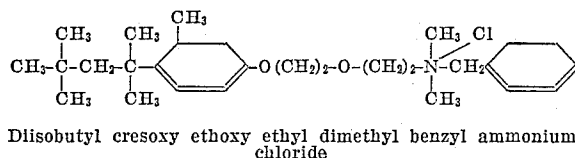


wherein R is an alkyl radical containing 6 to 20 carbon atoms, R₁ is a hydrogen atom or lower alkyl radical containing 1 to 6 carbon atoms, R₂ is an alkyl, aryl, or arylalkyl radical usually having 1 to 20 carbon atoms, R₃ is an alkyl, aryl, or an arylalkyl radical usually having 7 to 16 carbon atoms, Z is a halogen atom such as chlorine, bromine, iodine, or fluorine, and n is 0 or 1.

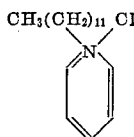
The compounds which we have found most useful and which are preferred for use in our invention have the Formula A wherein n is 1 and R₃ is a benzyl radical, such as:



and



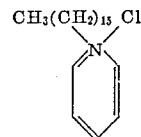
Other compounds within the scope of Formula A can also be used with good although somewhat less efficacious results than the preferred compounds, or compounds of Formula B can be used with good results as typified by



Lauryl pyridinium chloride

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and



Cetyl pyridinium chloride

Other compounds which also can be used in the treatment process of our invention include:

Cetyl dimethyl benzyl ammonium chloride
Cetyl trimethylammonium bromide
Octadecyl amine acetate
Lauryl trimethyl ammonium chloride
Acetyl chlorine bromide
Cetyl pyridinium fluoride

We have found that these and other quaternary ammonium salts as defined herein can be used in the aqueous treatment bath in the concentration range of .25 to 5.0% by weight based on the vehicle with a preferred range of .25 to 2.0%. They are usually used at a concentration of 1%. Although the treatment baths usually contain a single quaternary ammonium salt, they may also contain combinations of them in water or in water containing other materials to further condition the photographic element such as chemical buffering agents, formaldehyde, ethylene glycol and others.

The following examples illustrate typical uses of these compounds in our treatment baths.

EXAMPLE 1

Photographic paper prints were exposed, developed in a conventional manner, fixed in fresh acid fixer, washed for 5 minutes in water at 83° F., then soaked for 5 minutes in a 1% solution of diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride and air dried. The prints were then subjected to 6 days' storage under tropical conditions (98% relative humidity and 110° F.). Prints which received this treatment were unchanged in appearance from those prepared in the same manner but held at normal room temperature and humidity. These results were surprising since control prints processed in the same manner but without the special treatment were severely faded and stained in image areas by the tropical storage.

EXAMPLE 2

Photographic prints were prepared and treated in the same manner as in Example 1 except that artificially exhausted (3 g. of Ag⁺/l.) acid fixer was used in place of fresh acid fixer. Surprisingly, these prints showed no image fading and only a very slight yellowing in the non-image area after 6 days' storage under tropical conditions. Control prints showed severe fading and over-all yellowing after the same tropical storage.

EXAMPLE 3

Paper prints were prepared and processed in the manner used in Example 1 but a 1% solution of diisobutyl cresoxy ethoxy ethyl dimethyl benzyl ammonium chloride was used in place of the 1% solution of the compound of Example 1. These prints were found to be unchanged following the 6 day storage at elevated temperatures and humidity in contrast with the severe fading and yellowing that was produced in a control print by the same tropical storage.

EXAMPLE 4

Paper prints were prepared and processed in the same manner as in Example 1 in which a 1% solution of lauryl pyridinium chloride was substituted for the 1% solution of the compound in Example 1. Six days' storage at elevated temperature and humidity produced no stain or fading in these prints in contrast to the severe fading and staining produced in the control prints.

EXAMPLE 5

Twelve identical black-and-white prints were exposed from a normal negative. They were all given identical development in a conventional manner, then fixed, washed and treated as shown in Table I. After drying these 5 differently treated prints were exposed to accelerated fading tests by storing them at 110° F. and 98% R.H. for six days. A comparison of the results shown in Table I shows the advantages derived from the treatment of our invention.

Table I

ACCELERATED FADING TEST
[Six days' exposure at 110° F.; 98% R.H.]

Fixing conditions (acid fixer)	Wash time, min.	Control samples	Sample treated 5 minutes in a 1% solution of—	
			Diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride	Diisobutyl cresoxy ethoxy ethyl dimethyl benzyl ammonium chloride
Fresh.....	5	Severe fading and staining in the silver image area. Clear areas did not yellow.	Prints had normal appearance. (No yellowing or fading observed.)	Prints had normal appearance. (No yellowing or fading observed.)
Do.....	10	do.....	do.....	Do.
Exhausted (3 gms. Ag ⁺ /l)....	5	Severe fading in silver image area. Severe over-all yellowing.	No fading observed. Very slight yellowing in the non-image area.	No fading observed. Very slight yellowing in the non-image area.
Do.....	10	Slight fading in the silver image area. Moderate over-all yellowing.	do.....	Do.

EXAMPLE 6

Three identical black-and-white prints were exposed from a normal negative, developed in the conventional way, fixed in an artificially exhausted fixing bath and washed for five minutes. One print was then dried and used for a control. The other two prints were given a special five minute treatment prior to drying; one being treated in a 1% solution of lauryl pyridinium chloride, the other being treated in a commercial hypo eliminator containing hydrogen peroxide, and ammonium hydroxide dissolved in water. Table II demonstrates the advantages of our treatment over no treatment or the use of a conventional hypo eliminator.

Table II

ACCELERATED FADING TEST
[Six days' exposure at 110° F.; 98% R.H.]

Fixing conditions (acid fixer)	Wash time min.	Control samples	Sample treated for 5 minutes in—	
			1% solution of lauryl pyridinium chloride	Hypo eliminator containing hydrogen peroxide, ammonium hydroxide in water solution
Exhausted (3 gms. Ag ⁺ /l).....	5	Severe fading in the silver image area. Severe over-all yellowing....	No fading observed..... No appreciable yellowing.....	Considerable fading observed. Slight over-all yellowing.

The following example illustrates the effectiveness of the treatment bath in protecting prints from the effect of external strong sulfiding agents.

EXAMPLE 7

Photographic prints prepared and processed in the manner used in Example 2 were soaked for 3 minutes in a 0.2% sodium sulfide solution before drying. These treated prints were not stained by such exposure to a strong sulfiding agent.

Tests made on prints given the treatment of our invention have shown that without exception, fungal attack was reduced to a minimum and in many cases prevented entirely. The loss of the quaternary ammonium compound from the treated photographic element appears to proceed at an extremely low rate, thus insuring good protection of long exposure periods.

The treatment baths are equally effective when used on either projection or contact prints. When double-weight

paper is used, it is advantageous to lengthen the usual 5 minute treatment to 10 minutes.

Photographic black-and-white films, especially those coated with fine grain emulsions such as is commonly used for making microcopies of letters, blue prints, etc. are stabilized very effectively against image sulfiding and fungal attack when they are given a 2 to 5 minute treatment in a 1% solution of diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride following the normal fixing bath wash. A 1% solution of any of the other

quaternary ammonium salts of our invention may also be used to advantage.

30 The treatment of our invention is most advantageously used in the protection of black-and-white prints and films because sulfiding is primarily detrimental to silver images. Although color pictures are not as subject to the detrimental effects of sulfiding as black-and-white pictures, 35 since there is normally no silver image present, fungicidal protection is needed. The baths described can be used to advantage for the fungicidal protection they give.

Aqueous solutions of certain quaternary ammonium salts can be used very advantageously as a convenient and 40 effective treatment bath for protecting photographic ele-

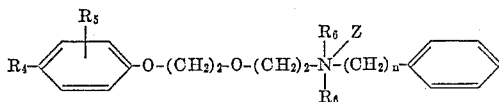
ments against chemical deterioration and microbiological attack under tropical storage conditions. The treatment consists of giving the photographic element being processed a short wash following the fixing bath with a 5 to 10 minute soak in an aqueous solution containing preferably from .25 to 2.0% of the quaternary ammonium salt before drying. Black-and-white prints or films containing appreciable amounts of residual thiosulfate compounds but which have been given the stabilizing and fungicidal treatment will not fade or yellow when stored under tropical conditions for prolonged periods and fungicidal attack is minimized and often prevented. This treatment is not only much more effective than prior art processes but is 60 convenient and simple. For example, multiple fixing baths, prolonged washing, or the use of toxic, unstable chemicals such as potassium permanganate, iodine, hydrogen peroxide and others are not needed in our process.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it 75

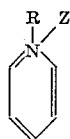
will be understood that variations and modifications can be effected within the spirit and the scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A process in which a developed and fixed silver image in a photographic element is (1) treated in an aqueous solution containing at least 0.25 percent by weight of a compound selected from the group consisting of surface active compounds of the formula:



and

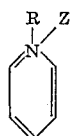


wherein R and R₄ each represents an alkyl radical having from 6 to 20 carbon atoms; R₅ and R₆ each represents a member selected from the group consisting of a hydrogen atom and a lower alkyl group having from 1 to 6 carbon atoms; n is an integer of 0 to 3; and Z is a halogen atom; and (2) then drying the treated element.

2. A process in which a developed and fixed silver image in a photographic element is (1) treated in an aqueous solution containing at least 0.25 percent by weight of diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride; and (2) is then dried.

3. A process in which a developed and fixed silver image in a photographic element is (1) treated in an aqueous solution containing at least 0.25 percent by weight of diisobutyl cresoxy ethoxy ethyl dimethyl benzyl ammonium chloride; and (2) is then dried.

4. A process in which a developed and fixed silver image in a photographic element is (1) treated in an aqueous solution containing at least 0.25 percent by weight of a surface active compound of the formula:

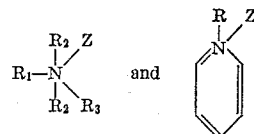


wherein R is an alkyl radical having from 6 to 20 carbon atoms and Z is a halogen atom; and (2) is then dried.

5. A process in which a developed and fixed silver image in a photographic element is (1) treated in an aqueous solution containing at least 0.25 percent by weight of lauryl pyridinium chloride; and (2) is then dried.

6. A process in which a developed and fixed silver image in a photographic element is (1) treated in an aqueous solution containing at least 0.25 percent by weight of cetyl pyridinium chloride; and (2) is then dried.

7. A process in which a developed and fixed silver image in a photographic element is (1) treated in an aqueous solution containing at least 0.25 percent by weight of a surface active compound of the formula:



wherein R, R₁, R₂, and R₃ are members selected from the group consisting of alkyl, aryloxyalkyloxyalkyl, aryl, and arylalkyl radicals, said radicals represented by R having 6 to 20 carbon atoms and said radicals represented by R₁, R₂, and R₃ having 1 to 20 carbon atoms; and Z is a member selected from the group consisting of halogen atoms, sulfate radicals, and acetate radicals; and (2) is then dried.

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