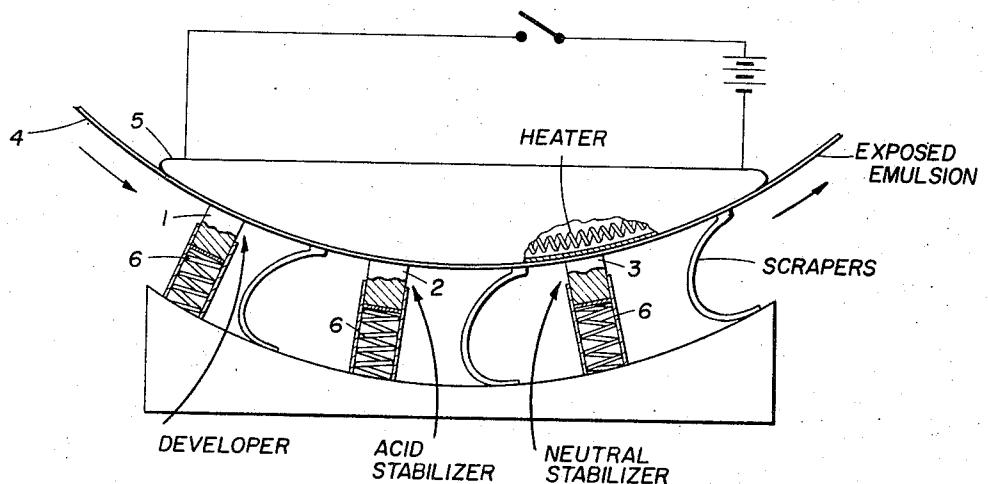


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SOLID HOMOGENEOUS COMPOSITIONS CONTAINING
SILVER HALIDE PROCESSING AGENTS
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1

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**SOLID HOMOGENEOUS COMPOSITIONS
CONTAINING SILVER HALIDE PROC-
ESSING AGENTS**

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This invention concerns a dry photographic processing method, more particularly, the use of a solid homogeneous composition containing a processing agent to develop or otherwise process an exposed light-sensitive silver halide emulsion.

Photographic materials normally require processing with a developing agent after which the light-sensitive element must then be treated to render it insensitive to light. Most of the processing systems involve the use of liquid baths such as aqueous alkaline solutions of a reducing agent as a developer followed by a fixing bath using a silver halide complexing agent. However, with the rapid increase of office copying, data recording, and information storage and retrieval systems, there has been an increasing demand for processing systems which do not involve the use of liquid baths with the attendant problems of keeping qualities, replenishing characteristics, difficulty in handling, etc.

Many substitute methods have been suggested for the use of liquid processing solutions. For instance, Land U.S. 2,616,804 describes viscous developers which contain sufficient moisture for processing. However, the viscous method is essentially a liquid method and requires a pod or similar method when applying the liquid material to the exposed element. In one embodiment where heat is employed, the heat is merely used to evaporate the moisture from the surface of the photographic element.

However, Zindler et al. German patent application 1,003,578 uses moisture released from water of crystallization. The use of moisture released from water of crystallization results in unavoidably leaving a crystal pattern in the photographic element. Moreover, the process is difficult to control since crystal hydrates tend to decompose when exposed to air. A further disadvantage of crystalline hydrates is that when stored under cyclic temperature conditions in the presence of excess moisture, as in a gelatin layer, solution and recrystallization tend to occur, resulting in the formation of very coarse crystal patterns. The same deficiencies apply to heterogeneous mixtures of crystalline material.

We have found a system of dry processing photographic materials employing a homogeneous solid material in which the moisture can be maintained constant and which can be used with greater facility than previously known methods, and gives a particularly uniform result.

One object of this invention is to provide solid processing components having a high degree of storage stability and ease in processing exposed photographic material. Another object is to provide a method of dry processing exposed photographic materials. A further object is to provide a homogeneous material containing a fixed amount of moisture uniformly dispersed in the solid ma-

2

terial which may contain a processing agent such as a silver halide developer, a fixing agent, etc. A still further object is to provide a solid block processing method which can be used with the employment of heat. Another object is to provide a processing web containing solid material having dispersed therein processing agents. Still another object is to provide a dry processing method which is subject to use with automated equipment.

The above objects are obtained by utilizing a fusible carrier material forming a composition solid at room temperature (about 20° C.) and melting below about 115° C., having incorporated therein water and one or more processing agents such as a developer, stabilizer, activator, fixing agent, etc.

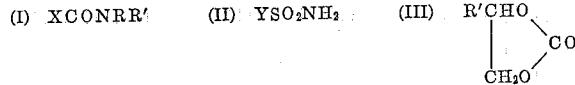
15 The carrier materials useful in our invention are chosen on the basis of their forming homogeneous compositions with the silver halide processing agents to be incorporated therein. Advantageously, these compositions melt between 20° C. and 115° C. The composition formed from the 20 carrier materials and the processing agents must be fusible, that is, must melt without decomposing such that a homogeneous layer of solution will be formed on the surface of such solid compositions when they are subjected to heat, as by contact with an externally heated 25 surface, or heat generated at the surface by friction as in rubbing, twisting, etc. Further the carrier materials must be miscible with water, such that sufficient ionization of the processing agents may occur.

30 The carrier materials most useful in our invention are alkylene oxide polymers known also as polyglycols. A polyethylene glycol having an average molecular weight of about 4,000 is sold as Carbowax 4000 by Union Carbide Company. Other alkylene oxide polymers having 35 molecular weights from 1,500 to 20,000 or greater can also be used. However, with the polyglycols having a high molecular weight, it may be desirable to add a small amount of low-weight glycol such as triethylene glycol as a plasticizer. The alkylene oxide polymers may be modified without destroying their usefulness for this process, provided that the modified material is compatible with useful proportions of water and of the processing chemicals. For example, mixed ethylene oxides and propylene oxide polymers may be employed, or derivatives such as esters, 40 ethers, amides, etc. may also be used. A partial list of 45 such derivatives is as follows:

Oleic ester polyethylene oxide—1000;
Nonylphenol ether polyethylene oxide—1145;
N-methylmyristylamino polyethylene oxide—1045;
Oleyl ether polyethylene oxide—1500;
N-methyl-n-dodecylamino polyethylene oxide—1145;
50 Pluronic F38 (a polypropylene oxide-polyethylene oxide block polymer) sold by Wyandotte Chem. Corp.;
55 Polyethoxyethyl-bis-sulfuric acid (M.W.=1500);
Polyethoxyethyl-bis-carboglutamic acid (Na salt)
(M.W.=1600).

Other materials which are solid at room temperature and 60 will form processing compositions having melting points below 115° C. include specific compounds, complexes, eutectics or mixtures of two or more compounds. In addition to melting within the most useful range, the preferred carrier materials are compatible with the processing chem-

icals and water present to give a homogeneous mixture, and do not interfere with the reaction. Beeswax and monostearin have been successfully employed as carriers. Organic acids melting in the correct range may be used as carriers for stop baths, fixing and stabilizing baths, etc. Particularly useful carrier materials are polar compounds having high dielectric constants containing the electron withdrawing groups $-\text{SO}_2-$ and $-\text{CO}-$ and may be represented by the following formulas:



where X may be chosen from the group consisting of H, alkyl groups of 1 to 4 carbon atoms, $\text{R}'\text{NH}-$, $\text{R}''\text{O}-$ and $-(\text{CH}_2)_n\text{CONRR}'$, where n is 1 to 4, R may be chosen from the group consisting of H, CH_3 , and $\text{HOCH}_2\text{CH}_2-$, R' may be chosen from the group consisting of H and CH_3 , R'' may be lower alkyl or 1 to 4 carbon atoms, X and R' together may be a diradical chosen from the group consisting of $-(\text{CH}_2)_a\text{CO}-$ and $-(\text{CH}_2)_b-$ where a is 2 to 3 and b is 3 to 5, R and R' taken together may complete a heterocyclic ring such as a morpholine or piperidine, Y may be chosen from the group consisting of alkyl groups of 1 to 4 carbon atoms NH_2- , $\text{R}''\text{O}-$, aryl and substituted aryl. The following are some examples of specific compounds included in these generic formulas:

formamide
acetamide
propionamide
N-methylacetamide
N,N-dimethylacetamide
N-(2-hydroxyethyl) acetamide
N,N'-bis(2-hydroxyethyl) malonamide
N,N'-bis(2-hydroxyethyl) adipamide
N,N'-bis(2-hydroxyethyl)-N,N'-dimethylsuccinamide
succinimide
valeramide
glutarimide
2-pyrrolidinone
2-oxohexamethylenimine
ethyl carbamate
urea
N-methylurea
N,N'-dimethylurea
sulfamide
methyl sulfamate
ethyl sulfamate
methylsulfonamide
ethylsulfonamide
p-Toluenesulfonamide
ethylene carbonate
propylene carbonate

These materials may be used alone or in combination with other materials, either as mixtures, complexes or eutectics. By the proper choice of mixtures of these compounds or mixtures of these compounds with many other compounds, many variables in processing such as processing temperature, rate of processing, maximum density, fog level, gamma, etc., can be adjusted as desired.

Some compounds included in the generic formulas are liquid at room temperature and while satisfactory for use in liquid processing baths would not be satisfactory in coatings of photographic elements. These compounds, on mixture with either other compounds covered by the generic formulas or many other types of compounds, will form mixtures which are solid at room temperature. Also some compounds with desirable carrier properties but with melting points too high for practical operating conditions can be used by mixture with other substances

which will lower their melting points. Mixtures illustrating some of these points are shown in the following table:

	Additive	M.P. of Additive (deg.)	Percent Additive Range to obtain M.P. of 100° or less
To succinimide, M.P. 123° C.			
Formamide	2	15-100	
Triethanolamine	21	35-100	
N-methylacetamide	25	22-100	
Ethyl carbamate	49	25-100	
Acetamide	79	16-100	
N,N'-dimethylurea	100	25-95	
N,N'-bis(2-hydroxyethyl)adipamide	130	48-78	
To urea, M.P. 132°			
N-(2-hydroxyethyl)acetamide	<25	44-100	
N-methylacetamide	25	40-100	
2-amino-2-methyl-1-propanol	25	57-100	
1,6-hexanediol	42	71-100	
Ethyl carbamate	49	61-100	
2,2,2-trichloro-1-ethoxy ethanol	51	45-100	
n-Butyl carbamate	53	86-100	
n-Propionamide	78	40-100	
Acetamide	79	30-100	
Imidazole	88	50-100	
Methylurea	99	30-100	
n-Valeramide	102	72-95	
2-amino-2-methyl-1,3-propanediol	109	38-95	
Succinimide	123	(1)	
N,N'-bis(2-hydroxyethyl)-adipamide	130	55-80	
Thiourea	171	30-45	
Lithium nitrate	255	13-23	

¹ None, but at 30%, forms a eutectic with M.P. 111° C.

30 As an alternative procedure, the carrier material may be used to form a complex with hydroquinone by heating the carrier material with hydroquinone and using the complex wherever the carrier material is used by itself. This is a particularly advantageous method of incorporating the material, since materials which are liquid at room temperature but which form complexes which are solid at room temperature can be used. Liquids which can be used include N-methyl-pyrrolidinone, acetylmorpholine, etc. The complex releases hydroquinone upon heating sufficiently to develop an exposed emulsion.

35 In a useful embodiment the solid material is coated in a thin layer of about 0.001 to 0.003-inch thickness on a support which is to be contacted against the silver halide emulsion. A preferred coverage for the carrier material is about 1-2 g./ft.², but a larger amount may be used with a binder provided the carrier material to binder ratio is from about 2:1 to 8:1. When used with the diffusion transfer process, this layer is coated over a nucleated receiving support, whereas, when used in the colloid transfer process, it is coated over an untreated receiver sheet or one which has thereon a fogging agent to increase the density of the transferred image.

40 In carrying out the diffusion transfer process, the exposed silver halide emulsion is contacted against a nucleated receiving sheet having the overcoat of this invention and containing therein a silver halide developer and a silver halide solvent. This sandwich is then heated to a temperature sufficient to melt the carrier material for a sufficient time for the emulsion to develop and the positive image to form in the nucleated layer. Supercooling occurs so that the carrier material remains liquid for some time after the melted layer has been cooled back to room temperature, facilitating removal of the receiving sheet from the emulsion layer. After transfer occurs, the receiving sheet is separated from the emulsion revealing a positive image.

45 In carrying out our process with a colloid transfer type emulsion, the tanning silver halide developer is preferably incorporated in the unhardened silver halide emulsion and contacted against the overcoated receiving sheet of this invention. The sandwich is heated to a temperature sufficient to melt the carrier material causing tanning development to occur in the silver halide emulsion. Upon removal from the heating source, the sandwich is separated, revealing a transferred stratum of un-

hardened emulsion on the receiving support. Successive copies can then be made.

The colloidal material which may be used in the diffusion transfer process as a vehicle for the light sensitive silver halide may be any of those capable of swelling, which can be used in photographic emulsions such as gelatin, polyvinyl alcohol, methyl cellulose, polyacrylamide, copolymer of ethylacrylate and acrylic acid, cellulose ether phthalate, albumin, collodion, etc. The vehicle used in the colloid transfer process is a colloid which can be hardened by a tanning silver halide developer.

The carrier material is preferably coated together on the support with a suitable film-forming binder to provide suitable adhesion to the support. Although a wide number of binders may be used, those which are particularly useful are flexible binders including those described above as suitable as vehicles for photographic emulsions, but also including binders, such as for example, a copolymer of ethylene and maleic acid, cellulose ethers such as ethyl cellulose, cellulose esters such as cellulose acetate butyrate and cellulose acetate containing approximately 33% acetyl, poly-N,N-diethylacrylamide, a copolymer of vinyl pyrrolidone and vinyl acetate, a copolymer of styrene and butadiene, proteins, such as casein and the like, etc., providing the binders are water permeable.

By the term, "silver halide processing agents," we means to include those chemicals commonly used for developing, activating, acidifying, fixing, stabilizing, toning, etc. of silver halide emulsions. The particular developing agents used are not critical, but include those commonly known as silver halide reducing agents such as, for example, N-methyl-p-aminophenol sulfate, ascorbic acid, hydroquinones, 3-pyrazolidones, including 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl - 3 - pyrazolidone, etc., p-phenylene diamine, catechol, stannous octoate, dextrin, 3,5-diaminophenol, etc.

The silver halide solvents or silver complexing agents which are useful include, for example, thioureas, thiocyanates, thiosulfates, mercapto-containing compounds such as mercapto acetic acid, quaternary ammonium salts, polyamines such as tetraethylene pentamine, etc.

The silver halide emulsion is preferably silver chloride, but other conventional developing out emulsions may be used such as silver bromide, iodide, bromochloride, bromoiodide, chloroiodide, chlorobromoiodide, etc.

It is preferable to use a paper receiving sheet but other supports may be used such as cellulose acetate, glass, wood, metal, polymeric materials, such as polyesters, polyolefins, and the like.

When the carrier material contains a developing agent, a solution is preferably made above the melting temperature of the carrier material and can be stored in a solid condition upon cooling. When the solution is used for developing an exposed silver halide emulsion, the solution may be used in the molten condition at a temperature above the melting point of the solution. It will be appreciated that various components used on conventional silver halide developing solutions can be incorporated.

When the carrier material containing the developing solution is used as an overcoat on silver halide emulsions, it may be used in a manner similar to that used with the colloid and/or the diffusion transfer silver halide emulsions. A barrier coat may be used if desired, to prevent migration of the developer from the carrier material layer into the silver halide emulsion prior to thermal processing of the exposed emulsion. The carrier material and/or developer may be incorporated in the silver halide emulsion for some purposes.

The carrier material is advantageously used in amounts sufficient to provide a homogeneous mixture of the developer and other materials present. When incorporated in a silver halide emulsion, the carrier material should be present at a concentration of at least 0.1 g. per milli-

mole of silver halide. When used in a layer over or under a silver halide emulsion, it is necessary to have a higher concentration of at least 0.4 g. per millimole of silver halide.

5 The temperatures at which development takes place are above the melting point of the carrier material. However, in some instances the temperature may be considerably higher depending upon the speed of development desired, hardness of the emulsion, type of developer used, etc. The upper limit is dependent upon these same factors.

10 In preparing the dry material, a solution of the processing chemical is prepared and stirred until homogeneous after which it is added to the molten carrier at a temperature above its melting point. In a preferred developer preparation, the developer-to-carrier ratio is 1:5. Of course, the proportions can differ widely depending upon the processing agents, the silver halide emulsion, the form used, etc.

15 The liquid carrier material containing the processing material can be cast into blocks and then pressed in contact with the exposed photographic emulsion and heated. Polyglycols are particularly useful in this embodiment. The carrier melts, releasing the processing agent to react with the photographic material. The absence of 20 processing fluid obviates the necessity of drying the processed photographic material. Moreover, the waxy surface results in an attractive product when this process is used with prints. In addition, since this processing method is rapid and does not require a drying step, it can be used 25 in data processing systems where the photographic result is required shortly after the exposure has been made.

30 The particular processing materials which may be incorporated in the carrier material depend upon the desired results. For instance, a 3-stage process might be used wherein a first block of carrier material containing developer is contacted against the exposed photographic elements with the application of heat. The next block might contain an acid stabilizer, whereas the third block could contain a neutral stabilizer. As an alternative, the 35 block might contain the components of a monobath so that the photographic element would be developed and stabilized by contacting against a single wax block.

35 In one embodiment, a Carbowax block melts at about 60° C. but is solid at room temperature (about 20° C.). During processing the temperature of the exposed light-sensitive element may range from about 60° C. to about 40 120° C. Development may be accomplished in as little as two seconds, but stabilization may require a longer time, possibly five to ten seconds. The use of two stabilizing blocks may facilitate the time balance so that the photographic element can pass through the process in a given length of time.

45 The processing chemicals which may be used for incorporation into the carrier material are not critical and may be a matter of choice. It will be appreciated, of course, that those which are incompatible with the carrier material so that a homogeneous mixture cannot be obtained are not within the scope of this invention. It will also be appreciated that wherein a polyglycol is an especially 50 useful material, certain other polymeric materials which are capable of holding a given amount of moisture in a homogeneous material which is solid at room temperature may also be used. For instance, hydroxy ethyl cellulose, carboxymethyl cellulose, etc., may be used for certain 55 purposes.

60 Moisture is preferred in the mixture of the carrier and processing agent and is included along with the processing agent in the molten mixture to disperse the processing agent in the polyglycol or similar carrier material. In 65 our preferred embodiment about 10% moisture based on the total weight of the mixture is used, but a range of 2% to 30% is useful.

70 The attached drawing shows one embodiment of our invention. Polyglycol solid blocks are prepared with a wax block 1 containing developer, wax block 2 containing an

acid stabilizer, and wax block 3 containing a neutral developer. The exposed silver halide emulsion on a support 4 is passed past a heating element 5 having a surface temperature about 200° F., each block is biased against the exposed silver halide emulsion on a support by means of spring 6. The scrapers 7 remove excess carrier material from the exposed emulsion.

The following examples are intended to illustrate our invention but not to limit it in any way.

EXAMPLE 1

Kodak Developer D-72 was dissolved in water to make a concentrated developer. This was thickened by the addition of hydroxyethyl cellulose and a thin layer was allowed to dry. Development of a silver halide contact paper was accomplished by applying heat to the hydroxyethyl cellulose layer by means of a flat iron set at low heat, about 65° C. A sharp image was obtained.

EXAMPLE 2

A hydroxyethyl cellulose layer was prepared as in Example 1, but using a hydroquinone-thiosulfate monobath containing 1-phenyl-3-pyrazolidone, in place of the solution. The paper used was a silver chloride emulsion of low silver content. Processing was accomplished by the application of heat as in Example 1. Development took about 1 minute and produced a stable image of good maximum density and fairly low minimum density.

EXAMPLE 3

Carbowax 1500 and Carbowax 4000 were each used as supporting media for the monobath which was of the following composition:

Imino-diethanol-SO ₂ adduct, 19% SO ₂ , grams	60.5
Imino-diethanol, grams	2.5
2-aminoethanol, grams	8.0
Sodium erythrobate, grams	10.0
4-methyl-1-phenyl-3-pyrazolidone, gram	1.0
Potassium bromide, grams	2.0
Sodium thiosulfate, pentahydrate, grams	10.0
Water to make, cc.	100.0

The amine monobath was dissolved in 500 grams of melted Carbowax and the wax layer was allowed to harden on a sheet of cellulose acetate. This was then placed in contact with a sheet of the exposed emulsion of Example 2 and heated with a flat iron at about 75° C. for about 30 seconds. The image formed was stable and had cleaner whites than the preceding example. The Carbowax layer was not sensitive to standing before use, neither losing moisture nor oxidizing.

EXAMPLE 4

The monobath in this case was the same as that in Example 3, except that the stabilizing agent was an amine thiosulfate rather than sodium thiosulfate. The amine thiosulfate was prepared according to U.S. 3,169,992 by substituting 2 grams of sulfur for the sodium thiosulfate in the above formula. Processing procedures were exactly the same as those above. The resulting image showed the same high quality and stability as that in Example 3. The image in Examples 3 and 4 was clearly visible through the cellulose acetate support, and it was not necessary to separate it from the support for viewing.

EXAMPLE 5

An amine developer, similar to the monobath of Example 3 but containing 2.0 grams sodium erythrobate, no sodium thiosulfate and no methyl phenyl pyrazolidone, was incorporated in Carbowax 4000 and coated over a sheet of the unexposed photographic paper of Example 2. The paper was exposed through the wax layer and was then heated with a flatiron. A low-contrast image was obtained. The image required fixation.

EXAMPLE 6

An amine developer similar to that of Example 5 but containing 4.0 grams hydroquinone and 1.0 gram 1-phenyl-3-pyrazolidone instead of sodium erythrobate, was incorporated in Carbowax 4000 (0.5 cc. developer per 2.5 grams Carbowax). This was coated upon a cellulose acetate sheet to give a dry, waxy layer. Upon heating in contact with exposed photographic paper, a sharp image was obtained. The image was stabilized by stripping off the developer layer and pressing the developed image into contact with a Carbowax layer consisting of 2.5 grams Carbowax 4000 + 0.50 cc. of an acidic 20 percent aqueous thiourea solution, also coated on an acetate support. The application of heat resulted in a light-stable image.

EXAMPLE 7

A monobath was prepared of the following composition:

2,4-diaminophenol dihydrochloride, grams	2.5
Iminodiethanolamine-SO ₂ , 19% SO ₂ , grams	60.0
Potassium bromide, grams	2.0
Thiourea, grams	7.0
Acetic acid, glacial, grams	25.0
Water to make, cc.	100.0

One cc. of this was incorporated in 2.5 cc. Carbowax 4000 and coated on a sheet of cellulose acetate. When this was heated for 60 seconds at 60° C. in contact with exposed photographic paper, a stable image of good contrast was obtained.

EXAMPLE 8

The amine developer in the Carbowax carrier of Example 6 was cast into a block. The hard waxy block was used to develop an exposed photographic enlarging paper by placing the paper, emulsion side up, on an aluminum plate heated to 180° F., and rubbing the emulsion with the developer block. After development was completed (approximately 30 seconds were required), the paper was stabilized by treating it in the same manner with a block containing a thiourea stabilizer similar to that of Example 6 but containing twice as much Carbowax 4000. This resulted in a light-stable image with a hard, smooth, glossy surface.

EXAMPLE 9

Sheets of paper coated with a silver halide emulsion of contact speed were overcoated with the Carbowax-developer composition of Example 6. The stabilizing composition of Example 6 was coated on the back of each of a number of sheets. The papers were then given an image-wise exposure and developed by placing the first sheet on the heated plate; when it developed, a second paper was placed on top which both developed in turn and stabilized the one beneath. This process was repeated. The quality obtained was very good.

EXAMPLE 10

Developing blocks were prepared using 5.0 grams of urea as the suspending medium. Various amounts of the following developer solution were incorporated into the melted urea.

Iminodiethanol-SO ₂ adduct, 19% SO ₂ , grams	60.5
Iminodiethanol, grams	2.5
2-aminoethanol, grams	8.0
Hydroquinone, grams	4.0
Phenidone, gram	1.0
Potassium bromide, grams	2.0
Water to make, cc.	100.0

After the blocks had cooled and solidified, they were placed in contact with the emulsion side of a sheet of recording paper containing a fine grain silver chloride

gelatin emulsion which was in contact with a heated plate at 120° C. The data below shows the results:

Sample No.	Amount of Dev. Solution (ml.)	Melting Point of Block (° C.)	Results
Control	0.0	130	No processing.
1	0.5	115	Slow development; 30 sec.
2	1.0	110	Rapid development; 2 sec.
3	1.5	104	Do.
4	2.0	102	Do.
5	3.0	90	Block tends to be soft. Rapid development; 2 sec.

EXAMPLE 11

Developing blocks were prepared by adding various amounts of developer solution to 10 grams of acetamide.

Developer solution

	Grams
Methylaminoethanol	4.0
Methylaminoethanol-SO ₂ adduct, 18% SO ₂	71.0
1-phenyl-4,4-dimethyl-3-pyrazolidone	.7
Hydroquinone	22.0
Water	17.0

The solid blocks were used to develop a recording paper containing a fine grain silver chloride gelatin emulsion as in Example 10, using a heated block at 200° F.

Sample No.	Amount of Dev. Solution (ml.)	Melting Point of Block (° C.)	Results
Control	0	79-80	Rapid development, 15 sec.
1	1	70-72	Rapid development, 8 sec.
2	2	60-65	Rapid development, 8 sec.

EXAMPLE 12

The procedure described above for Example 11 was repeated, using succinimide in the place of acetamide. The results are shown below:

Sample No.	Amount of Dev. Solution (ml.)	Melting Point of Block (° C.)	Results
Control	0	123-124	
1	1+0.5 HOH	90-105	Slow development; 60 sec. good image.
2	2	90-105	Slow development; 40 sec. good image.

EXAMPLE 13

The procedure of Example 12 was followed using 10 grams of acrylamide in place of the succinimide. The following results were obtained:

Sample No.	Amount of Dev. Solution (ml.)	Melting Point of Block (° C.)	Results
Control	0	84-86	
1	1+1 H ₂ O	~50	Good development; 10-20 sec.
2	2	~50	Do.

EXAMPLE 14

The procedure of Example 13 was followed using 10 grams of urethane in the place of succinimide. The results are shown below:

Sample No.	Amount of Dev. Solution (ml.)	Melting Point of Block (° C.)	Results
Control	0	50	
1	1+1 H ₂ O	30	Good development; 10-20 sec.
2	2	37	Do.

Dimethylurea and p-toluene sulfonamide were also used successfully as the suspending media. The p-toluene sulfonamide produced complete dense images in periods of 1-5 seconds at 200° F. Other solid materials which have been used are 2,2-diethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol, and 2-butyne-1,4-diol.

EXAMPLE 15

Urea and dimethylurea, urea and Carbowax, and urea and urethane were employed. The mixtures of urea and urethane were especially good. For example, a mixture which contained 5 grams of urea, 5 grams of urethane, and 1 gram of the developer described in Example 11, had a freezing point of about 85° C., and produced a dry, white uniform, firm solid.

Other addenda

Phenylmercaptotetrazole, benzotriazole, nitroindazole, sodium antraquinone sulfonate, potassium bromide and various antifoggants may be incorporated into the processing blocks. In particular, the incorporation of a small amount of diethylaminoethanethiol is effective in keeping fog levels low.

Successful stabilization has been achieved by wax block processing with more than a dozen compounds of differing structure. Details and results of the work are given below.

EXAMPLE 16

A silver halide enlarging paper having a low silver emulsion was used for all of the tests.

In each instance, three blocks were used—one containing developer, one with stop, and a third with stabilizer. Blocks were of Carbowax 4000 containing 10% added water plus chemical agent.

The developer block contained:

	Grams
Hydroquinone	4.3
Methylaminoethanol	12.4
Sulfur dioxide	2.56
Phenylmercaptotetrazole	0.5
Carbowax 4000	100.0
Water	10.0

The stop block contained:

	Grams
Acetic acid	10.0
Carbowax 4000	100.0
Water	10.0

The stabilizer block comprised Carbowax and the different chemicals under test. Concentrations were between 2.5-20.0 grams per 100 grams Carbowax.

Processing was at 200° with 15 seconds for development, 10-second stop and 30-second stabilizer.

The processed strips were tested for stability by exposing to strong light. If stable, they were further tested at 94% R.H. for 3 days at 100° F.

Materials and results

Thiourea.—Gives pure whites and high stability to light.

5-(2-hydroxyethyl)tetrahydro-s-triazine-2-[1H]-thione.—Capable of producing good whites of high light stability.

Guanidinium-3-mercapto-propanesulfonate.—Produces very good light stability and moist incubation stability with minimum loss of density.

S-β-aminoethylisothiuroniumbromide.—Produces images of good light stability. The corresponding amino-propyl- and ethylaminoethyl-compounds acted similarly.

Thioglycerol.—A promising stabilizer imparting light stability and fairly good moisture stability.

Cysteine.—Introduces good stability, including moist incubation stability.

A substituted *thiovaleric acid* gave good light stability. *Quaternary salts* which effected stabilization included

11

α -picolinium- β -phenylethyl bromide, tetrapropyl, tetraethyl, and tetramethyl bromides, preference in this order. These compounds give clear whites of good light stability.

EXAMPLE 17

Activation and stabilization of emulsions containing developing agents was accomplished with blocks containing 100 grams of Carbowax 4000, 20 grams of methyl-amino ethanol (as an alkali), 10 cc. of water and:

Grams 10

Thioglycerol ----- 6

or

Guanidinium-3-mercaptopropane sulfonate ----- 10

When a coating containing incorporated developing agent was treated for 30 seconds at 90° C. with the developing block described above, clearly legible line images were obtained. These were stable to prolonged exposure to light. This coating consisted of a medium-grain silver bromoiodide emulsion containing 1.1 mole percent iodide was coated on a paper base at a coverage of 144 mg. silver and 398 mg. gelatin/ft.². Incorporated in the emulsion were:

Grams

3,6-dihydroxybenzonorbornane ----- 103.0

Sodium bisulfite ----- 132.0

1-phenyl-3-pyrazolidone per mole of silver ----- 6.5

EXAMPLE 18

Clearly legible images were produced with the emulsion of Example 17 by using activator blocks of the following composition:

Grams

Methylaminoethanol ----- 20

Water ----- 10

Carbowax 6000 ----- 100

Such processing is particularly suited for recording oscillograph traces where prolonged exposure to light is not involved.

EXAMPLE 19

The polyethyleneglycols (Carbowaxes) used as the suspending media in Examples 3-9, may be modified in a number of ways without destroying their usefulness for our process. For example, varying quantities of propylene oxide may be inserted in the molecule, as is done in the series commercially known as Pluronics (Wyandotte Chemicals Corp., Wyandotte, Michigan). One hundred grams of Pluronics F-38, F-77 and F-88 were used to replace the Carbowax 4000 in the developer block of Example 16. The composition of these Pluronics is indicated as follows:

Pluronic No.	Percent Propylene Oxide	Percent Ethylene Oxide	Approx. Mol. Wt.
F-38-----	20	80	9,750
F-77-----	30	70	6,500
F-88-----	20	80	11,250

All of these developer blocks were firm solids. The same silver halide emulsion as in Example 16 was developed by applying the blocks for periods of 20 and 30 seconds at approximately 95° C. Strong development was obtained in every case. The paper was then stabilized using blocks of the following composition:

Pluronics F-68, F-77 or F-88, grams ----- 100
Thiourea, grams ----- 20
Water, cc. ----- 10
Acetic acid, cc. ----- 10

Portions of the above blocks were caused to melt on the surface of the developed prints. Stabilization took place within 30 seconds. The prints were very stable to subsequent exposure to light.

12

EXAMPLE 20

The developer block and processing were identical to those of Example 19, except as suspending media: (a) monostearin and (b) beeswax were employed. Strong images were obtained in both cases.

EXAMPLE 21

The following developer was prepared: To 100-gram quantities of molten Carbowax 4000, 20, 30, 40, and 50 cc. quantities of Solution A were added.

Solution A

2-methylaminoethanol sulfur dioxide adduct, 17.8%

SO ₂ , grams	100.0
1-phenyl-4-methyl-3-pyrazolidone, grams	4.5
Hydroquinone, grams	11.0
1-phenyl-5-mercaptopotetrazole, gram	0.048
Sodium thiosulfate, pentahydrate, grams	10.0
Water to make, cc.	400.0

20 Methylaminoethanol was added to adjust the pH to 11.0

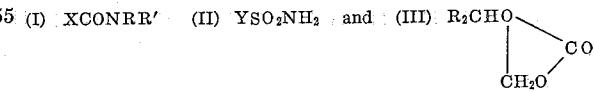
This developer, while in the molten state, was coated upon receiver sheets containing Carey Lea silver. A fine-grain positive photographic film was exposed to a suitable object and contacted with the coated receiver sheet on a plate heated to 95° C. The developer layer melted causing development of a negative image in the film and transfer of a positive image to the receiver sheets. Particularly good transfer was obtained in the receiver coated with the mixture containing 40 cc. of Solution A per 100 grams of Carbowax. Similar results were achieved using receiver sheets nucleated with nickel sulfide nuclei. Other nucleation agents might also be used.

30 The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

35 While the foregoing examples have illustrated the processing of positive images on photographic papers, it will be recognized that our processing system is applicable to negative systems, reversal systems, color, etc.

We claim:

1. A homogeneous composition comprising a water-miscible organic compound carrier selected from the group consisting of alkylene oxide polymers, hydroxyethyl cellulose, carboxymethyl cellulose, monostearin, beeswax, mixtures of alkylene oxide polymers with propylene oxide and mixtures of alkylene oxide polymers with ethylene oxide, organic acids, and polar compounds having high dielectric constants containing the electron withdrawing groups $-\text{SO}_2-$ and $-\text{CO}-$ represented by the formulas:



wherein X is selected from the group consisting of H and alkyl groups of 1 to 4 carbon atoms, $\text{R}'\text{NH}-$, $\text{R}'\text{O}-$ and $-(\text{CH}_2)_n\text{CONRR}'$ and radicals

$-(\text{CH}_2)_a\text{CO}-$ and $-(\text{CH}_2)_b-$

forming a diradical with R' ; a is 2 to 3 and b is 3 to 5; n is 1 to 4; R is selected from the group consisting of H, $-\text{CH}_3$ and $\text{HOCH}_2\text{CH}_2-$; R' is selected from the group consisting of H, $-\text{CH}_3$ and radicals forming a heterocyclic ring with R; R_2 is selected from the group consisting of H and $-\text{CH}_3$; R' is selected from the group consisting of lower alkyl radicals and radicals forming a heterocyclic ring with X; and Y is selected from the group consisting of alkyl radicals having 1 to 4 carbon atoms, NH_2- , $\text{R}'\text{O}-$ and aryl radicals; a silver halide photographic processing agent; and about 2% to about 30%, by weight of said carrier, of water, said composi-

15

containing about 2% to about 30%, by weight of said carrier, of water, at a temperature at which said homogeneous composition is liquid.

16. A method of stabilizing an exposed silver halide emulsion comprising contacting said emulsion with a homogeneous composition which is solid at about 20° C. and melts at below about 115° C. comprising a silver halide stabilizing agent and an alkylene oxide polymer carrier containing about 2% to about 30%, by weight of said carrier, of water, at a temperature at which said homogeneous composition is liquid.

5

10

16

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C. E. DAVIS, *Assistant Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

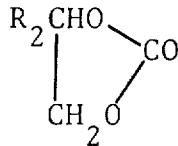
Patent No. 3,347,675

October 17, 1967

Richard W. Henn et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 28, for "means" read -- mean --; column 13, line 45, for "(I) XCONRR" read -- (I) XCONRR'--; line 55, for "H, CH₃" read -- H, -CH₃ --; line 73, for "oxide" read -- oxide --; column 14, formula III at the top of the page, should appear as shown below instead of as in the patent:



line 11, for "-(CH₂)_aCO-" and (CH₂)_b-" read -- -(CH₂)_aCO- and -(CH₂)_b --; same column 14, line 61, for "CH₃" read -- -CH₃ --.

Signed and sealed this 19th day of November 1968.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents