United States Patent Office 3,467,519
Patented Sept. 16, 1969

3,467,519

SWELLING REDUCTION TREATMENT FOR THE ACCELERATED PROCESSING OF GELATIN PHOTOGRAPHIC MATERIALS

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No Drawing. Filed Apr. 15, 1966, Ser. No. 542,762
Int. Cl. G03c 5/26
U.S. Cl. 96—50 9 Claims

ABSTRACT OF THE DISCLOSURE

Drying of processed photographic silver-halide-gelatin emulsions is speeded by treating processed wet emulsion with acid aqueous solution of aliphatic or aromatic sulfonic acid or aliphatic or aromatic sulfate, which compounds have more than 5 carbons.

The invention relates to baths which inhibit swelling for treating exposed and developed photographic materials, so that processing can be accelerated by shortening the drying time.

For use as protective colloid for photographic layers, the melting point or melting temperature of the gelatin must be increased. This can, in principle, be achieved by applying four different kinds of agents: water extracting agents (deswelling substances), agents which prevent swelling (hydrophobic agents), substances which precipitate gelatin and substances which tan gelatin. While the first three possibilities can be regarded as physical methods of reducing the swelling, the last method causes an irreversible chemical change of the gelatin structure. If water is extracted from the swelled gelatin layer by placing the layer in an alcoholic solution or concentrated salt solution, the reduced swelling is not maintained when the layers are again placed in pure water. The process is reversible. Heavy metal salt solutions which can form high molecular weight hydroxy salts, such as aluminum-, chromium-, trivalent iron-, cerium and uranyl salts act in a different way. The deswelling and hardening produced by them is irreversible since chemical complexes are formed.

By the use of the known chemical hardening agents such as formalin, triacryloformal, divinylsulfone and mucochloric acid, the gelatin layers are cross-linked so that the melting point is increased. After several months storage, the layers become horny and more brittle. This is termed after-hardening. When slow-acting hardening agents are added, it is therefore necessary that the layers can be permeated by treatment baths even after a considerable storage time. In photography it is customary to use as small a quantity of hardening agents as possible, especially in the case of highly sensitive emulsions where the reduction in permeability to development baths would immediately cause reduction in the sensitivity. The same applies to X-ray films. If the layers are only slightly hardened, the swelling remains high and the surface easily damaged during processing.

These disadvantages can be suppressed in many different ways. For example, hardening agents such as glutaric dialdehyde, may be added to the developers. It is necessary in such an application to use hardening agents that are as active as possible, which agents must be stable in alkaline solution. A special hardening bath (e.g., formalin solution containing alkali carbonate) may also be interposed during processing either before or after development. The hardening which results is irreversible. Reversible deswelling is obtained with concentrated alkali metal salts. A slightly acid solution is usually employed.

It is among the objects of the present invention to provide methods for reversibly hardening developed gelatin layers, whereby the swelling capacity of the layer is immediately reduced.

It has now been found that the swelling of unhardened or slightly hardened photographic gelatin-containing layers with or without silver halide can be greatly reduced if the layers are treated for a short time with dilute aqueous solutions of substituted or unsubstituted aliphatic or aromatic sulfonic acids or sulfates having more than 5 C-atoms and preferably not more than 20 carbons, at a pH of 1 to 6, preferably 2 to 3. Examples of such compounds include oleyl sulfate, nonyl sulfate, alkyl sulfonic acids such as decylsulfonic acid, unsubstituted or substituted benzene sulfonic acids such as phenol sulfonic acids, unsubstituted or substituted naphthalene sulfonic acids such as naphthalene trisulfonic acid, naphthsultone -(1,8)-sulfonic acid-(3), and polymerized sulfonic acids such as polystyrene sulfonic acid, preferably having a molecular weight of up to about 3000.

When the baths according to the invention are employed, the swelling is immediately reduced and reaches a minimum after 1 to 2 minutes. Since the solutions are highly diluted, the baths can also be used after washing. A considerable reduction in the drying times is achieved since owing to the reduced swelling, the quantity of water to be evaporated is smaller.

The baths according to the invention are preferably used after development of the exposed silver halide emulsion layers, preferably at the end of the entire processing operation. No further treatment is required after the swell inhibiting bath according to the invention. Even washing is not necessary. The baths according to the invention contain about 5 to 50 g., preferably 10 to 20 g./l. of the sulfates or sulfonic acids. The required pH is obtained by addition of organic or inorganic acids such as formic acid, acetic acid, hydrochloric acid.

The baths are very stable and do not lose their activity for a long time. The moist photographic layers are left in the bath for 1 to 2 minutes. They acquire a leathery handle and no longer feel slimy. Excess solution can be removed from the treated material with a sponge. The materials dry about twice as quickly as the untreated samples. In a particular embodiment, the developed materials can be briefly rinsed with water or washed since the deswelling, in contrast to that obtained with salts, is only eliminated after prolonged exposure to water. The effect immediately disappears if the layers are subsequently treated in an alkaline bath. Deswelling is strictly reversible and the baths according to the invention thus differ fundamentally from chemical hardening agents.

Example 1

An exposed photographic film which is suitable particularly for X-ray photography and which contains a silver halide gelatin emulsion layer on both sides of a support of triacetyl cellulose is processed according to common practice in the following baths:

(1) Development bath—development time 5 minutes:

	G.
p-Methylaminophenol	3
Sodium sulfite sicc.	90
Hydroquinone	7
Potassium carbonate	50
KBr	5

Water up to 1 l.

(2) Fixing bath—treatment time 5 minutes:

	G.
Sodium thiosulfate cryst.	250
Sodium meta-bisulfite	50

Water up to 1 l.

(3) Wash with water—15 min.

At the end of the development times, the vertical swellings are measured in each case with a layer thickness measuring instrument. Samples of the above film processed in the identical way are then treated for 1 to 4 minutes in different deswelling baths.

Preparation of the baths

To a solution of 20 g. of glacial acetic acid in 1 l. of water are added 10 g. each of the following compounds:

(1) Naphthol-sulfonic acid-(7)
(2) Lauryl sulfate
(3) Decyl sulfonic acid
(4) Diphenylsulfonic acid
(5) 4-hydroxy-3-carboxy-2-nitrodiphenylsulfone-sulfonic acid-4'
(6) Naphthosultone-(1,8)-sulfonic acid-(3)
(7) 2-hydroxycarbazole-sulfonic acid-(7)
(8) Polystyrene sulfonic acid (low molecular weight M=1300)
(9) Oleyl sulfate
(10) Pyrene tetrasulfonic acid
(11) Percaptobenzthiazole sulfonic acid
(12) Naphthalene trisulfonic acid
(13) Phenolsulfonic acid
(14) 5-nitrobenzene disulfonic acid-(1,3)
(15) Dinaphthylmethane sulfonic acid
(16) Dibutyl-naphthalene sulfonic acid
(17) Oleic acid-N-methyltauride

Result

The following swellings of the untreated layers are observed:

(1) Photographic film dry: 10μ.
(2) After development: 37μ.
(3) After fixing: 60μ.
(4) After washing with water: 85μ.

The washed material is then placed directly into the baths described above for 1–4 minutes and in each case the swelling is determined after 1 minute.

	Swelling in μ after a time of action of—			
	1'	2'	3'	4'
Substance:				
Compound 1	27	17	15	15
Compound 2	43	38	35	34
Compound 3	56	48	38	33
Compound 4	32	23	20	20
Compound 5	25	15	15	15
Compound 6	32	24	20	20
Compound 7	34	20	15	15
Compound 8	45	37	33	30
Compound 9	34	----	----	34
Compound 10	37	----	----	31
Compound 11	38	20	20	20
Compound 12	44	41	33	33
Compound 13	32	----	----	32
Compound 14	44	----	----	35
Compound 15	53	45	41	35
Compound 16	48	35	27	25
Compound 17	34	----	----	35

Thus, in the most favourable case, swelling of the layers is reduced in the baths from about 80–90μ to 15–20μ. The layers are leathery and not easily damaged.

Example 2

A photographic element having a silver halide gelatin emulsion layer processed as in Example 1 is treated, after washing with water, with a bath of the following composition:

Bath 1:

Ageprun (wetting agent, trademark of Agfa-Gevaert AG)	cc 5
Acetic acid	cc 20
Naphthol-(I)-sulfonic acid	g 10
Water to make up to 1 l.	

After 4 minutes, the films are treated with a 4% sodium carbonate solution.

Swelling is measured at intervals of 1 minute.

After treatment in:	Swelling in μ
Water—15 min.	88
Bath 1:	
After 1 minute	30
After 2 minutes	17
After 3 minutes	17
After 4 minutes	17
4% sodium carbonate solution:	
After 1 minute	91
After 2 minutes	92
After 3 minutes	110

The intensive deswelling (from 88 to 17μ) is immediately eliminated if treatment is followed by an alkaline bath, a proof of the reversibility of the process.

Example 3

If the above-mentioned swelling-reducing substances are added to a bath at the end of the entire processing operation, the photographic layers dry considerably more quickly than after the usual washing with water. To shorten the drying times of photographic materials, a hardening bath is generally employed. The hardening bath is usually combined with the fixing bath to form a so-called hardening-fixing bath. However, the common hardening-fixing baths have the disadvantage that they are not stable over prolonged periods, especially at elevated temperatures, since due to the reaction of the hardening agent, e.g., of the aluminum salt with sodium thiosulfate, the hardening-fixing bath becomes cloudy due to deposition of aluminum hydroxide and sulfur. Moreover, layers which are hardened with aluminum salt are brittle and make retouching more difficult.

All these disadvantages are avoided by the use of one of the baths according to the invention as an after-treatment bath. These baths are stable and the deswelling of the layer can be reversed by washing with water so that no difficulties occur in retouching.

The drying times are shown on the right in the following table. For comparison there are given the drying times obtained when using a 2% aqueous acetic acid solution and a hardening-fixing bath of the following composition:

Hardening-fixing bath:

Water	cc 1000
Sodium thiosulfate	g 200
Sodium sulfite sicc.	g 20
Glacial acetic acid	cc 15
Potassium alum	g 10

TABLE

	Drying times			
	Without washing	With subsequent washing with water		
	0	1'	3'	5'
Dibutylnaphthalene sulfonate	18'	19'	22'	23'
Naphthalene sulfonic acid-(1)-sodium	19'	21'	22'	27'
4-hydroxy-3-carboxy-2-nitrodiphenyl-sulphone-sulfonic acid-4'	13. 5'	13'	15'	20'
Naphthol-(1)-sulfonic acid-(2)	15'	19'	19'	23'
2% acetic acid solution	38'	35'	35'	35'
Hardening fixing bath	28'	----	----	----

A film which contained a silver bromide gelatin emulsion layer on a support of acetyl cellulose was used as photographic material. The relative air humidity was 55% at the time of the measurements. The table shows that the effect of the final bath can be eliminated by sufficiently long washing with water.

Example 4

In the same way as described in Example 3 a highly sensitive photographic film having a silver bromide gelatin emulsion layer containing about 5 moles percent of silver

iodide was tested. After exposure, the film was developed with a developer of the following composition:

Water ---------- cc--	750
p-Methylaminophenol ---------- g--	2
Sodium sulfite sicc. ---------- g--	100
Hydroquinone ---------- g--	5
Borax ---------- g--	2
Water up to 1 l.	

	Drying times, min.
Dibutylnaphthalene sulfonate ----------	32
Naphthalene sulfonic acid-(1)-sodium ----------	30
4-Hydroxy-3-carboxy-2-nitro-diphenylsulfone-sulfonic acid-(4') ----------	20
Naphthol-(1)-sulfonic acid-(2) ----------	22
2% acetic acid solution ----------	>50
Hardening fixing bath ----------	29
Acid fixing bath ----------	40

The hardening fixing bath had the same composition as in Example 3. The composition of the acid fixing bath was as follows:

Water ---------- cc--	1000
Sodium thiosulfate ---------- g--	200
Potassium metabisulfite ---------- g--	20

The relative air humidity was 55%. The substances were used in the same concentration as in the previous example, i.e., the solutions contained 1% of active substance.

The various films become more or less cloudy as a result of the treatment in these after-treating baths. This cloudiness disappears completely after drying.

We claim:

1. A process for reducing the swelling of gelatin photographic layers including the step of contacting an exposed, developed and fixed photographic silver-halide-gelatin layer with an 0.5 to 5% aqueous solution of an aliphatic or aromatic sulfonic acid or an aliphatic or aromatic sulfate, said acid or sulfate having more than 5 carbon atoms and said solution having a pH of between 1 and 6.

2. A process as defined by claim 1 in which after the contacting the silver-halide-gelatin layer is dried without further treatment.

3. A process as defined by claim 1 in which after the contacting the silver-halide-gelatin layer is washed for less than a minute and then dried.

4. A process as defined in claim 1, wherein the exposed, developed and fixed photographic gelatin layer is contacted with an aqueous solution of a benzene or a naphthalene sulfonic acid.

5. A process as defined in claim 1, wherein the exposed, developed and fixed photographic gelatin layer is contacted with an aqueous solution of polystyrene sulfonic acid.

6. A process as defined in claim 1, wherein the exposed, developed and fixed photographic gelatin layer is contacted with an aqueous solution of 4-hydroxy-3-carboxy-2-nitro-diphenylsulfone-sulfonic acid-4'.

7. In the processing of photographic silver-halide-gelatin film, the improvement according to which the film is exposed, developed and fixed, and the swelling of the gelatin layer is then reduced by contacting the layer with a 0.5 to 5% aqueous solution of an aliphatic or aromatic sulfonic acid or an aliphatic or aromatic sulfate, said sulfonic acid or sulfate having more than 5 carbon atoms, the solution having a pH of 2 to 3.

8. The combination of claim 7 in which the contacted film is subsequently dried without further treatment.

9. The combination of claim 7 in which the contacted film is subsequently washed for less than a minute and dried.

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U.S. Cl. X.R.

96—111