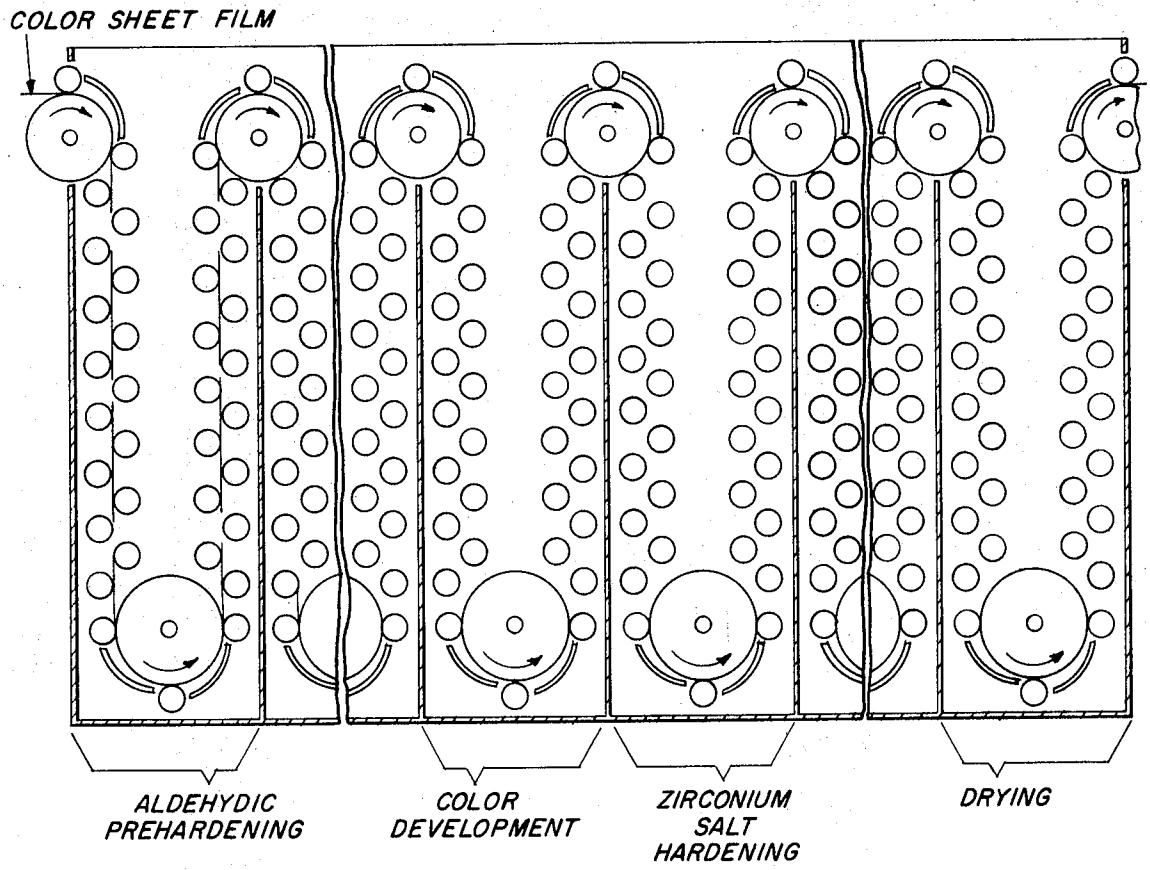
June 1, 1971 F. R. HOLLY, JR., ET AL 3,582,347

PROCESSING MULTILAYER PHOTOGRAPHIC COLOR FILMS

Filed July 5, 1968



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United States Patent Office 3,582,347 Patented June 1, 1971

3,582,347

PROCESSING MULTILAYER PHOTOGRAPHIC COLOR FILMS

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Filed July 5, 1968, Ser. No. 742,574
Int. Cl. G03c 1/30
U.S. Cl. 96—111 13 Claims

ABSTRACT OF THE DISCLOSURE

A process for development of multilayer photographic color products involves progressively hardening the layers with an aldehydic prehardening solution, and after development, in an acidic zirconium salt solution. The process reduces damage to the product in continuous processing machines.

This invention relates to the processing of multilayer photographic color products particularly in continuous processing machines at elevated temperatures so as to obtain a processed and dried film in about 10 minutes time.

Multilayer photographic elements for color photography usually contain at least three differently sensitized silver halide emulsion layers usually one being sensitive to the red region of the spectrum, another to the green and the third to the blue region of the spectrum. The blue sensitive layer may be coated outermost on a support and separated by a yellow filter from the green and red sensitive emulsion layers. In the incorporated coupler elements the emulsion layers or layers adjacent thereto contain color-formers or coupler compounds in which case the layers are color-developed with developing solutions containing color developing agents of the p-phenylenediamine type. The elements may be processed to color negatives by initially developing with color developer solutions or reversal processed to color positives by first developing with a black-and-white developer and subsequently with a color developer. The preparation of multilayer elements of this type is disclosed, for example, in Jelley and Vittum U.S. Pat. 2,322,027 and Mannes et al. U.S. Pat. 2,252,718.

The emulsion layers of the above photographic elements which usually contain gelatin, when wet with the processing solutions, swell and become soft and are, therefore, readily abraded and deformed. Accordingly, the emulsion layers are commonly hardened as much as possible by the time they have been coated upon the support. Since this amount of hardening is usually not sufficient to prevent abrasion and other defects, especially when using machine processing methods, a common method involves pretreating an exposed photographic element just before development with a prehardening solution, for example, containing an aldehyde such as formaldehyde. While formaldehyde solution has been considered useful in prehardening gelatin emulsion layers, high concentrations of formaldehyde, such as on the order of about 55 grams per liter of the prehardener solution, have ordinarily been neecssary to adequately harden gelatin. Baden and Bard U.S. Pat. 3,220,849 describe the use of formaldehyde together with succinaldehyde as the hardening agents in a prehardener solution. Bard U.S. Pat. application Ser. No. 591,142, filed Nov. 1, 1966 now Pat. 3,451,817 uses acidic compositions containing formaldehyde together with a bis-bisulfite adduct of a dialdehyde, such as succinaldehyde, glutaraldehyde and derivatives thereof, for prehardening exposed multilayer color products. However, these prehardening methods and other methods using, for example, aluminum salt hardeners are by themselves not adequate for processing at elevated temperatures and when using machine processing methods for reasons given below.

It is known to process photographic elements at elevated temperatures of the order of 100 to 125° F. thereby materially shortening the processing cycle. However, as the temperature is raised, the hydrophilic emulsion layers, especially gelatin emulsion layers, of the photographic elements soften and swell to a great extent and are very easily abraded or deformed. Thus, the swollen layers are easily damaged while being transported from one processing solution to another, by hand or in racks and particularly when using continuous processing apparatus such as roller transport apparatus to advance the photographic elements through the various solutions whereby contact with the rollers and other objects damages the layers. Little is known of methods for processing and drying multilayer color products at elevated temperatures especially in roller transport apparatus adapted to continuous processing. The mentioned aldehyde prehardening solutions aid in preventing emulsion damage in processing. However, it is found that even when the above aldehyde prehardener solutions are used, one result is that repeated contact of the edges and surfaces of the emulsion layers with apparatus such as rollers and guides causes pieces of the swollen emulsion layers to separate from the support and be deposited on the film as "dirt." This is especially true in processing sheet color film where the edges of the sheet repeatedly strike the rollers and guides causing "skiving" of the emulsion, i.e. small pieces of emulsion break away at the edge of the sheet. Also, increased temperature may cause the layers to stick to the rollers in the processing solutions or in the drying chamber or the sheets to stick to each other in the drying chamber. In some cases, the result is that the processed emulsion has an "orange peel" surface apparently due to contact of the emulsion surface with rollers in a drying chamber. Accordingly, it was necessary to find new hardening methods for use in processing multilayer color products at elevated temperatures especially when using continuous processing apparatus and methods as will appear from the following description of the invention.

We have discovered that the multilayer color elements can be satisfactorily hardened, especially for handling at elevated temperatures of the order of 100–125° F. in processing apparatus such as racks or roller transport apparatus, by progressively hardening the emulsion layers after exposure and before development with an aldehyde solution so as to increase the hardness and limit the swelling of the emulsion layers, and after development of the emulsion layers further hardening the layers with an acidic solution of a zirconium salt. In negative color processes the acidic zirconium salt solution is preferably employed just after the color development step and when the solution also contains a silver halide solvent, it functions as a hardening-stop-fix solution as illustrated in Example 1 below. In reversal color processes the acidic zirconium salt solution can be used, for example, before or after the reversal color development step as a hardening-stop solution, or when the acid zirconium salt solution also contains silver halide solvent, the solution can be used as the final fixing solution as described in Example 3 below. The process of the invention involving first aldehydic prehardening and then zirconium salt hardening is very useful for hardening multilayer color products in roll or sheet form; however, when the sheet product is to be processed at the elevated temperatures, for example, in roller transport apparatus adapted to continuous processing, both a zirconium salt hardening agent and an aluminum salt hardening agent is useful particularly to prevent the mentioned skiving effect. It has further been found that in the second hardening step following development the zirconium salt cannot be replaced by an

aldehyde hardener or an aluminum salt hardener. The zirconium salt or both zirconium salt and aluminum salt are necessary to obtain the desired progressive hardening. The combination of the zirconium and aluminum salts provides an unexpected type and degree of hardening such that the emulsion layers withstand the effects of machine processing at elevated temperature. As a result, it is possible to completely process and dry color films or papers in about 10 minutes compared to previous processes requiring as long as two hours.

The progressive hardening process of the invention using the aldehydic and zirconium salt solutions can be employed in color processes in which the color film or paper is conveyed in racks from solution to solution, the aldehyde and zirconium hardening solutions reducing damage to the emulsions in rack processing. However, the hardening process is preferably used when carrying out the color processes in continuous processing apparatus, such as shown in the drawings, to reduce or eliminate damage to the emulsions such as the mentioned skiving or sticking of the emulsions. The continuous processing apparatus used depends somewhat on the type and form of the particular color product being processed. The accompanying drawings show in schematic form a very useful roller transport processing apparatus in which continuous processing of sheets or lengths of color film can be carried out. As shown, the film is advanced between driven staggered rolls through the solutions to a drying chamber. U.S. Pat. 3,025,779 describes in detail a self-threading roller transport processing apparatus of this type. When sheet film contacts the guides and rollers as shown, there is a tendency for the mentioned emulsion skiving to take place. In the drying chamber as the color products advance when incompletely hardened emulsion surfaces contact the rollers, they may dry to an orange peel surface or one sheet of film may come into contact with the stick to another sheet of film. As mentioned, the progressive hardening process of the invention reduces or eliminates these problems. It will be seen that in the drawings a number of the tanks used in the processes of Examples 1 and 3 have been omitted for simplification of the description.

The color processing can be carried out in roller transport processing apparatus in which rollers are positioned usually only at the top and bottom of the tanks so color film or color paper can be advanced in a sinuous path through the tanks. When motion picture color film is being continuously processed, a series of spools or recessed rollers may be arranged in the tanks and so the film takes a helical path around the spools or rollers as it is advanced in the tanks and to a drying chamber in a well-known manner. The examples below illustrate color processes which are preferably carried out in the mentioned continuous processing apparatus.

The solution of aldehyde used in prehardening and limiting the swelling of the color products is preferably acidic and can contain only an aldehyde as the hardening agent especially formaldehyde in which case about 100–200 ml. of 37% formaldehyde per liter is useful.

When a dialdehyde is used with formaldehyde, about 0.5 to 10 grams of the former and about 5–15 grams of the latter per liter are useful. A preferred aldehyde solution for use in the process is an aqueous solution of pH about 2 to 7 of a mixture of formaldehyde and a bis-bisulfite adduct of a dialdehyde, particularly those in which the aldehyde groups are separated by a linear chain of 2 to 3 carbon atoms which chain has no more than 3 substituents thereon other than hydrogen, said substituents being alkyl and/or alkoxy of from 1 to 4 carbon atoms. Included among these dialdehyde bis-bisulfite adducts used to advantage according to our invention are the bis-bisulfite adducts of the following dialdehydes: β-methyl glutaraldehyde, glutaraldehyde, α-methyl glutaraldehyde, maleic dialdehyde, succinaldehyde, cyclopentanedicarboxaldehyde, methoxy succinaldehyde, α,α-dimethyl glutaraldehyde, α,β-dimethyl glutaraldehyde, methyl succinaldehyde, α-methyl-β-ethoxy-glutaraldehyde, α-butoxy glutaraldehyde, β-isopropoxy succinaldehyde, butyl maleic dialdehyde, etc. The adduct of succinaldehyde is especially useful. The dialdehydes include those having the formula

$$OHC(—CHR_1)_n—X—(CHR_1)_n—CHO$$

wherein R_1 groups may be the same or different and represent hydrogen or lower alkyl, n is 1 to 2, X is oxygen, sulfur or selenium or $=NR_2$ where R_2 is hydrogen or lower alkyl. Representative dialdehydes of this class are:

Thio-bis-acetaldehyde	$OHC—CH_2—S—CH_2—CHO$
Chlorohydrate of N-methylamino-bis-acetaldehyde.	$OHC—CH_2—\overset{\overset{H}{\vert}}{\underset{\underset{CH_3}{\vert}}{N^+}}—CH_2—CHO\ Cl^-$
Imino-bis-acetaldehyde	$OHC—CH_2—NH—CH_2—CHO$
Oxy-bis-acetaldehyde	$OHC—CH_2—O—CH_2—CHO$
Seleno-bis-acetaldehyde	$OHC—CH_2—Se—CH_2—CHO$

When the bisulfite adducts of these dialdehydes are used with formaldehyde in the prehardener compositions, about 2 to 56 grams formaldehyde and about 1 to 100 grams of dialdehyde bisulfite adduct per liter are useful. However, it should be understood that the optimum amount of formaldehyde and of the adduct will vary with the degree of prehardening desired with the particular color product in use and the hardening activity of the aldehyde-bisulfite adduct in use. The concentrations are particularly useful with color films having gelatin emulsion layers. The prehardener compositions can be used with other hydrophilic colloid emulsion layers but are less effective. The adducts can be incorporated into the prehardener solutions in the form of the alkali metal or nitrogen base (ammonium or amine) salts.

The use of the formaldehyde-dialdehyde bisulfate adduct pre-baths results in a significant reduction in the odor of dialdehyde such as succinaldehyde which is characteristic of pre-hardener solutions prepared from the dialdehyde per se or dialdehyde precursor such as 2,5-dimethoxytetrahydrofuran. More particularly, just the right amount of preliminary hardening and swelling of the emulsion layers is obtained. Furthermore, relatively little formaldehyde is required compared to using formaldehyde alone. The prehardening step is generally designed in order to control the amount of swell of the emulsion layers from the dry thickness to the range of from about 100% to about 300% measured at the end of the color development step in the negative color process or at the end of the black-and-white development step in the reversal color process.

The percent swell is conveniently measured by an instrument for continuously measuring the swell of gelatin in photographic film coatings which is described by F. N. Flynn and H. A. Lavine in "Photographic Science and Engineering," volume 8, page 275 (1964). This instrument hereinafter will be referred to as "swelling meter."

Magnesium sulfate-formaldehyde-aldehyde bisulfite prehardener compositions especially useful and illustrated in the examples are disclosed in the Donivan U.S. patent application Ser. No. 595,353, filed Nov. 18, 1966 now abandoned. Magnesium sulfate alone or together with other salt such as sodium sulfate has the advantage of not readily crystallizing from solution onto the rollers or walls of the tanks of the processing apparatus.

The action of the zirconium salt-aluminum salt solutions used following prehardening and development of the multilayer color products appears to be unique. The solution is not replaceable by an acid aluminum salt solution such as a conventional hypo aluminum fixing solution as will be seen from the following examples. The solution

is not useful as the prehardening solution. The solution appears to coact with the aldehyde prehardened and developed emulsion layers to produce emulsion layers having the proper resistance to the frictional effects of the rollers and guides of the processing apparatus so that roller patterns are not observed and the emulsions do not separate from the edge of the film base. Also, sticking of the emulsion surfaces especially in a hot drying chamber is avoided.

A variety of water-soluble zirconium salts can be used, especially with emulsion layers containing a major amount of gelatin, for example, simple zirconium salts such as zirconium sulfate and zirconium nitrate, and complex salts such as zirconyl sulfate (presumably having the formula $H_2ZrO(SO_4)_2 \cdot 3H_2O$), zirconium ammonium sulfate, zirconium sodium sulfate, etc. However, zirconyl sulfate is preferred.

A variety of water-soluble aluminum salts can be used with the zirconium salt, especially when the emulsions primarily contain gelatin, for example aluminum chloride and nitrate, potassium aluminum sulfate, etc. However, aluminum sulfate is preferred.

As mentioned, the zirconium salts are especially useful in solutions following the color development of color processes. Zirconium salt such as zirconyl sulfate can be used, for example, in concentrations of about 2 to 10 grams per liter when processing at 100° F. Aluminum salts such as aluminum chloride can be used with the zirconium salt in concentrations of about 5 to 15 grams per liter for 100° F. processing. The concentrations are varied to obtain the desired degree of hardness, for example, depending upon the temperature of processing and whether roller transport processing is to be used. A useful combination is about 2 grams zirconyl sulfate with about 9 grams of aluminum sulfate. The pH of the zirconium salt solutions may be adjusted with strong acid such as sulfuric acid to a range of about 3 to 6. A pH of 4.0 is very useful. The solution can be buffered as usual using sodium acetate and acetic acid as illustrated in the examples. The thiosulfate in the zirconium salt solutions is not critical and can be alkali metal or ammonium thiosulfate.

The use of the aldehyde prehardener compositions with the zirconium and zirconium-aluminum salt hardening compositions in processing multilayer color products is illustrated in the following examples.

The following aldehyde prehardener solutions can be used.

PREHARDENER I

Sodium sulfate ____ g	150.0
Formaldehyde ____ g	10.0
Acetic acid, glacial ____ cc	1.7
Sodium bromide ____ g	2.0
Succinaldehyde ____ g	1.0

Water to 1 liter.
Sodium hydroxide as required to give pH about 4–7.

PREHARDENER II

	G.
Succinaldehyde	10.0
Sodium acetate	10.0

Water to 1 liter.

PREHARDENER III

	G.
Succinaldehyde bis-bisulfite	11.42
Sodium sulfate anhydrous	85.72
Sodium acetate, anhydrous	25.14
Sodium diacetate	0.29
Magnesium sulfate heptahydrate	240.00
Formalin, 37%	33.33

Water to 1 liter.
Adjust to pH 6.3.

Example 1.—Negative color processing

An incorporated coupler multilayer color film is provided comprising red, green and blue sensitive gelatin-silver halide emulsion layers on a support, a yellow filter being coated between the blue and green sensitive emulsion layers. The emulsion layers contain reactive methylene and phenolic coupler compounds reactive with p-phenylenediamine developing agents to form dyes of color complementary to the sensitivity of the respective layers. The film has about 1,500 mg. of gelatin per square foot on the emulsion side and the rear surface of the film base is coated with a thin blue dyed gelatin antihalation layer. The film base is either cellulose acetate or linear polyester.

The film in sheet or roll form is exposed to a colored subject and processed to a color negative in the steps and under the conditions below in a roller transport system such as shown in the drawings and U.S. Pat. 3,025,779 having staggered driven rollers which advance the film through a series of tanks containing the solutions and to a drying chamber.

	Sec.
Prehardener (100° F.)	80
Neutralizer (100° F.)	40
Developer (100° F.)	160
Stop-fix (100° F.)	40
Wash (100° F.)	40
Bleach (100° F.)	40
Fix (100° F.)	40
Wash (100° F.)	40
Posthardener (100° F.)	40
Wash (100° F.)	40
Dry (120° F. to 160° F.)	85

PREHARDENER

Prehardener Formulas I, II or III above.

NEUTRALIZER

Hydroxylamine, carbohydrazide, etc., aldehyde neutralizing solution such as shown in columns 4 and 5 of Blackmer and Vogt, U.S. Pat. 3,168,400.

DEVELOPER

	G.
Benzyl alcohol	5.02
Sodium bromide	1.17
Sodium hydroxide, 50% soln.	19.66
Sodium sulfite	1.88
Borax (pentahydrate)	33.00
Sodium hexametaphosphate	2.50
4-Amino-N-ethyl-N-[β-methane-sulfonamidoethyl]-m-toluidine sesquisulfate monohydrate	4.75

Water to 1 liter.
Adjust to pH 10.47.

STOP-FIX

Part A

	G.
Water	7.92
Ammonium thiosulfate, 58% soln.	215.00
Sodium sulfite	11.20
Acetic acid, glacial	20.00
Sodium hydroxide	9.00

Part B

	G.
Water	7.20
Zirconyl sulfate	2.12
Aluminum sulfate, 25% soln.	34.06

Parts A and B are mixed and diluted to 1 liter with water.
Sulfuric acid to pH 3.6 to 4.6.

BLEACH

Potassium ferricyanide-potassium bromide-boric acid solution adjusted to pH 7.9.

FIX

Ammonium thiosulfate-sodium bisulfite-sodium sulfite solution adjusted to pH 6.5.

POSTHARDENER

Acid-formaldehyde solution.

When the film is processed under the above conditions, the aldehydic prehardener is effective to partially harden and limit the swelling of the emulsion layers to the extent that dye images of the required sensitometric properties are obtained in the layers and the emulsion surface is not deformed in the neutralizing and developer steps. The subsequent use of the acid zirconyl sulfate-aluminum sulfate step further hardens the emulsion layers with the result that the emulsion layers of sheet film do not break away from the film base due to contact with the rollers and guides of the processing machine. Also, roller pattern is not observed in the processed element. The post-hardener is not always necessary but can be used to give the emulsions a final hardness to facilitate drying. Also, the neutralizer composition is not always required but is preferred in those cases where there is a tendency for the aldehyde of the prehardener to adversely affect color development of the emulsion layer. For example, some couplers tend to react with formaldehyde carried into the developer in which case the neutralizer can be used. In place of hydroxylamine sulfate, semicarbazide, hydrazine, carbohydrate, biuret, aminoguanidine, methylsemicarbazide and water-soluble salts of said compounds can be used as described in U.S. Pat. 3,168,400.

EXAMPLE 2

The film described in Example 1 is processed in the same manner except omitting the zirconyl sulfate from the stop-fix. As a result, the emulsions are damaged by contact with the apparatus and particles thereof appear in the solution and on the surface of the film. Also, the film tends to stick to rollers in the drying chamber and sheets of the film tend to stick together when they happen to come into contact.

Example 3.—Reversal color processing

An exposed film of the type described in Example 1 in sheet or roll form is processed in a roller transport system such as shown in the drawings or U.S. Pat. 3,025,779 in the following steps at 90–125° F. The film has about 1,432 mg. gelatin per square foot on the emulsion side and a gray antihalation layer is placed between the emulsion layers and the support.

PREHARDENER (150 sec., 95° F.)

Prehardener Formulas I, II or III above.

NEUTRALIZER (75 sec., 97° F.)

Hydroxylamine, carbohydrazide, etc. aldehyde neutralizing solution such as shown in columns 4 and 5 of Blackmer and Vogt, U.S. Pat. 3,168,400.

FIRST DEVELOPER (150 sec., 100° F.)

Sodium hexametaphosphate	g	2.0
N - methyl - p - aminophenol sulfate	g	6.0
Sodium sulfite, anhydrous	g	50.0
Hydroquinone	g	6.0
Sodium carbonate, monohydrate	g	35.0
Potassium bromide	g	2.0
Sodium thiocyanate	g	1.5
0.5% solution of 6-benzimidazole nitrate	cc	12.0
0.1% solution of potassium iodide	cc	10.0

Water to 1 liter.

FIRST STOP (75 sec., 100° F.)

	G.
Sodium acetate, anhydrous	3.58
Acetic acid, glacial	28.85

Water to 1 liter.

WASH (75 sec., 90° F.)

COLOR DEVELOPER (150 sec., 110° F.)

Benzyl alcohol	cc	6.0
Sodium hexametaphosphate	g	2.0
Sodium sulfite, anhydrous	g	5.0
Sodium carbonate, anhy.	g	40.0
Potassium bromide	g	0.25
0.1% solution of potassium iodide	cc	10.0
Sodium hydroxide	g	6.5
4 - amino - N - ethyl - N - [β-methanesulfonamidoethyl] - m - toluidine sesquisulfate monohydrate	g	11.33
Ethylenediamine sulfate	g	7.8
Citrazinic acid	g	1.5
t-Butylamine borane	g	0.1

Water to 1 liter.

SECOND STOP (75 sec., 110° F.)

	G.
Sodium acetate, anhydrous	3.58
Acetic acid, glacial	28.85

Water to 1 liter.

WASH (75 sec., 90° F.)

BLEACH (75 sec., 110° F.)

Potassium ferricyanide-potassium bromide such as shown in column 7 of U.S. Pat. 3,266,895.

FIX (75 sec., 110° F.)

Ammonium thiosulfate, 58%	cc	163.0
Sodium bisulfite, anhydrous	g	11.0
Boric acid	g	8.0
Acetic acid, glacial	cc	19.0
Sodium hydroxide	g	8.0
Zirconium sulfate·tetrahydrate	g	5.0

Water to 1 liter.

Adjust to pH 4.0.

WASH (75 sec., 90° F.)

DRY (150 sec., 125° F.)

As a result of reversal processing roll or sheet film in this manner, the emulsions are not damaged, they adhere well to the support and do not stick to each other or to machine surfaces in the drying chamber. In this process, it may be desirable to incorporate the zirconium salt or both zirconium and aluminum salts in the first or second stop solution to progressively increase the hardness of the emulsion layers as the film passes from solution to solution. Thus, with roll film, zirconium salt can be used in the stop or fixing solutions and with sheet film aluminum salt is advantageously used with the zirconium salt. Aluminum salt alone usually does not give adequate hardening.

Example 4

The color film of Example 3 is processed to a color negative and progressively hardened in the roller transport apparatus such as shown in the drawing in a 10-minute dry to dry cycle at about 100° F. by subjecting the film to the prehardening, neutralizing and color development steps of Example 1 followed by acid stop and wash steps, acid ferricyanide-bromide bleaching of the silver, fixing with zirconium sulfate composition as in Example 3, washing and drying. The resultant film is not deformed or otherwise damaged in the process.

U.S. Pat. 3,141,771 may be referred to for a detailed description of the useful components of the multicolor elements useful in the process of the invention including representative, e.g. cyan, magenta and yellow couplers for the emulsion. U.S. Pat. 2,322,027 and 2,252,718 provide procedures for the preparation of representative sensitive elements. The sensitive elements described in U.S. 2,252,718, not containing couplers, are reversal processed with coupler-containing developer solutions as described in U.S. 2,252,718, the ferricyanide bleach step preferably

being followed by fixing with a zirconium salt solution such as shown in Example 3 above. The reversal process of Example 2, U.S. 3,141,771 can also be used, a zirconium salt solution also being employed following the last color development step.

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.

We claim:

1. In a negative or reversal photographic color reproduction process wherein a color product having superposed silver halide emulsion layers is exposed to a subject and processing includes the development of colored images in the emulsion layers and the removal of undeveloped silver halide and silver images from the emulsion layers, the improvement for progressively hardening the emulsion layers during processing comprising treating the exposed emulsion layers before development with a solution of an aldehyde increasing the hardness of the layers, and after development of the emulsion layers further hardening the layers with an acid solution containing a hardening amount of a zirconium salt hardening agent.

2. The process of claim 1 wherein the zirconium salt solution also contains a hardening amount of an aluminum salt hardening agent.

3. The reversal color process of claim 1 wherein the zirconium salt solution is employed following the color development step.

4. In a negative photographic color reproduction process wherein a color product having superposed silver halide emulsion layers and color-forming compounds is exposed to a subject, colored images are developed in the emulsion layers and the undeveloped silver halide and silver images removed from the layers, the improvement for progressively hardening the emulsion layers during processing comprising (1) treating the exposed emulsion layers before development with a solution of aldehyde increasing the hardness of the layers, (2) developing colored images in the layers in the region of exposure by means of color-forming development and (3) further hardening the emulsion layers with an acidic solution containing a hardening amount of a zirconium salt hardening agent.

5. In a photographic color reproduction process wherein a multilayer color product having superposed gelatin-silver halide emulsion layers and color-forming compounds is exposed to a subject and processed by roller transport through a series of processing solutions including solutions for color-development and removal of silver and silver halide from the layers, the improvement for progressively hardening the emulsion layers during processing comprising (1) treating the exposed emulsion layers before development with a solution of aldehyde increasing the hardness of the emulsion layers, (2) developing the exposed emulsion layers and (3) further hardening the emulsion layers with an acidic solution containing a hardening amount of a zirconium salt hardening agent.

6. The process of claim 5 wherein color product is processed in sheet form and the acidic solution of zirconium salt further contains an aluminum salt hardening agent.

7. The process of claim 5 wherein the processing temperature is in a range of about 90 to 125° F.

8. In a photographic color reproduction process wherein a multilayer color product having superposed gelatin-silver halide emulsion layers containing color-forming compounds is exposed to a subject and processed in sheet form by roller transport through a series of processing solutions including solutions for color development and removal of silver and silver halide from the layers, the improvement for progressively hardening the emulsion layers during processing comprising (1) treating the exposed emulsion layers before development with a solution of aldehyde increasing the hardness of the emulsion layers, (2) developing colored images in the emulsion layers by means of color-forming development and (3) fixing and further hardening the emulsion layers with acidic solution containing a silver halide solvent, hardening amounts of a zirconium salt hardening agent and of an aluminum salt hardening agent.

9. The process of claim 8 wherein the color development step produces a multicolor negative image in the emulsion layers.

10. The process of claim 9 wherein the acidic fixing solution contains zirconyl sulfate and aluminium sulfate.

11. The process of claim 5 wherein development of the exposed layers is first carried out to produce only silver images therein and is followed by color development, and the acidic solution of zirconium salt is a fixing solution also containing silver halide solvent.

12. The process of claim 1 wherein the acidic aldehyde solution contains at least one member of the group consisting of formaldehyde, a dialdehyde gelatin hardening agent, and a bis-bisulfite of said dialdehyde.

13. The process of claim 12 wherein the step of treatment of the emulsion layers with the aldehyde solution is followed by treatment with an aldehyde neutralizing solution.

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