June 30, 1953 J. Q. UMBERGER 2,643,950

PROCESS OF TRANSFERRING AN IMAGE-BEARING GELATIN LAYER TO ANOTHER FILM BASE

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FIG. 1.

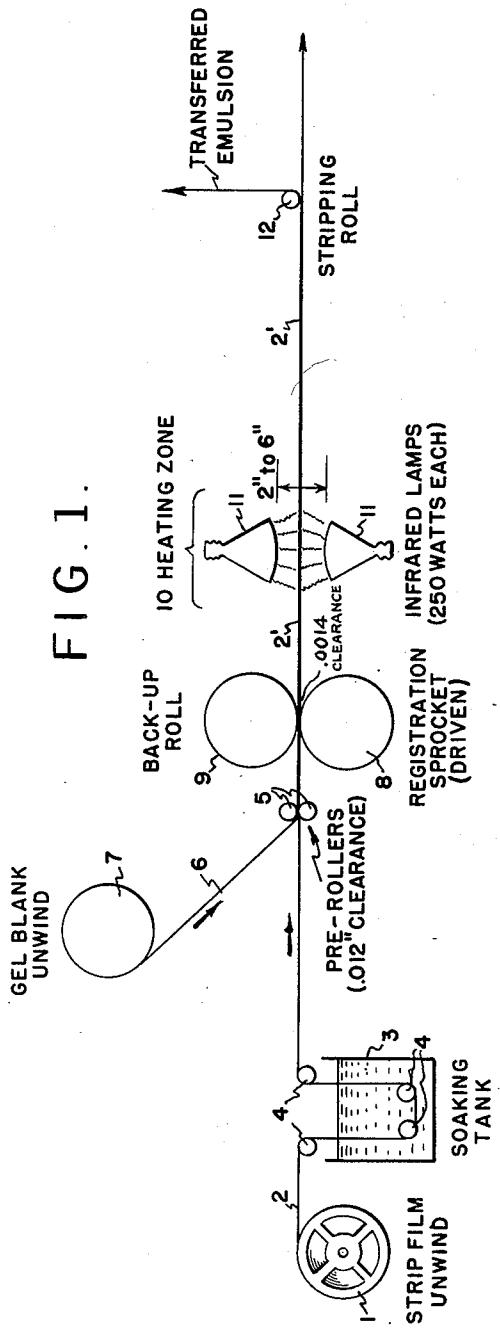


FIG. 2.

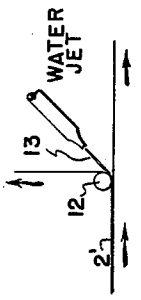
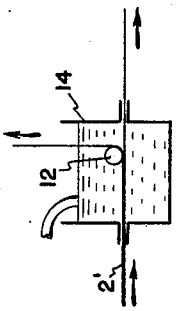


FIG. 3.



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PROCESS OF TRANSFERRING AN IMAGE-BEARING GELATIN LAYER TO ANOTHER FILM BASE

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10 Claims. (Cl. 95—2)

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This invention relates to photography and more particularly it relates to a process of transferring a colloid silver halide emulsion layer or silver image-bearing layer to a blank film having an outer layer composed of a thermally-reversible colloid. Still more particularly it relates to such a process wherein the adherence between the blank film and the silver halide layer or silver image-bearing layer is improved by a heating step.

An object of this invention is to provide improvements in the art of stripping layers from photographic elements and transferring them to another base. Another object is to provide such a process wherein the anchorage between the transferred layer to the new base is enhanced. A further object is to provide a simple and economical process for improving the anchorage between a perforated blank film and the removable colloid silver halide or silver image-bearing layer of a perforated motion picture stripping film. Still other objects will be apparent from the following description of the invention.

Various type of stripping films are known which consist of a water-permeable, thermally-reversible colloid-silver halide emulsion layer which is releasably joined to a support such as a cellulose derivative, e. g., cellulose nitrate, cellulose acetate, cellulose propionate, cellulose acetate butyrate, etc., a superpolymer, e. g., a polyvinyl acetal or a super polyamide (nylon); baryta coated paper, metal glass, etc., or to another colloid silver halide emulsion layer or other water-permeable colloid layer on such a support by means of a water-soluble or other adhesive. The outer water-permeable colloid or image-bearing layer is generally transferred after exposure and, in some cases, after developement and fixing to a blank film. The colloid is generally composed of gelatin. The blank film generally consists of a thin, flexible film base which has superimposed thereon a thin gelatin layer which may contain a hardener, e. g., chrome alum, dimethylol urea, etc., and/or an acid, e. g., acetic, lactic, citric, sulfuric, etc., or a base, e. g., sodium hydroxide depending on the pH desired. The two gelatin layers of the respective films are pressed into contact and the image-bearing layer is stripped from its original support.

It has been found that the anchorage between the colloid surfaces of the blank film and the colloid image-bearing layer of the photographic stripping element, e. g., stripping film can be

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markedly improved by applying heat in the form of infra-red radiation to the combined stripping and blank films between the registration operation and the stripping operation. The temperature during this heating stage should not be excessive, but yet sufficient to impart a slight tackiness to the surface of the thermally-reversible colloid and/or reduce the viscosity of the stripping layer.

In a further aspect of the invention a new stripping film has been developed which facilitates the transfer stripping operation. This film contains a colloidal material which is strongly absorptive of infra-red radiations in the stripping layer. The film is illustrated in Example V below.

In the case of transfer and stripping operations for perforated motion picture film, it has been difficult to secure adequate adherence in the area of the film perforations. It has been discovered that the adherence in such areas can be markedly improved by giving the light-sensitive film elements an extra exposure, e. g., a flash exposure to light, in the vicinity of the perforations, following which the film is developed, fixed, washed and dried. The heating with infra-red then follows while the blank film and the stripping film are in registration contact. The flash exposure causes fogging of the light-sensitive silver salts and the infra-red rays produce an increased localized heating in such areas thereby causing a higher degree of adherence at the edges than is obtainable without such prefogging.

An alternative method of improving the adherence in the areas adjacent the film perforations is by using a blank film which contains colloidal particles of infra-red absorbing materials including colloidal metals, e. g., silver, lead, antimony, bismuth, copper, etc., or colloidal carbon.

A practical manner of carrying out the processes just described will now be outlined with reference to the accompanying drawing wherein:

Fig. 1 is a schematic view in elevation of an apparatus.

Fig. 2 is a schematic view in elevation of a modified stripping device.

Fig. 3 is a schematic view of another modified stripping device.

Referring now to the drawing a reel 1 of an exposed front film or stripping film 2 of the type described in Jennings U. S. Patent 2,462,503 is passed through a tank 3 which contains an aqueous solution of one or more surface active agents and has its pH adjusted within a range

of 1 to 4.5. The film is directed during its passage by means of a series of guide rollers 4. It then passes between a pair of rollers 5 where it meets and is placed in approximate registration contact with a gelatin blank film 6 which unwinds from a roll 7. The gelatin surface of the blank film is lightly pressed into contact with the gelatin surface of the stripping film 2. The two films then pass through a registration device which, as shown in the schematic modification of the device, consists of a relatively large sprocket wheel 8 and an interfitting back-up roll 9. The two films 2 and 6 are pressed into exact registration contact in this device. The combined film 2' is then passed through a heating zone 10 where the temperature is adjusted so that the gelatin surfaces of the films blend together and the emulsion-transfer is facilitated. In the embodiment shown, this is accomplished by means of infra-red lamps 11 which are disposed above and below the film element in its line of travel. The film then passes to a stripping roll 12 where the blank film with the adherent outer image-bearing layer is stripped from the remaining image-bearing layer on the original film base. This is accomplished in Fig. 1 by passing the combined film over a stripping roll 12 in air. The film containing the transferred emulsion layer and the original film with its emulsion layer pass separately to different stations where they can be washed, dried and/or separately processed to silver images if this has not already been done.

The process is, of course, useful in transferring an exposed stripping film which has already been developed, fixed, washed and/or dried before the registration transfer is effected. The separate image bearing layers can be intensified to the proper degree of contrast after stripping in the event that the film has already been processed to silver images before the stripping transfer operation.

The stripping films of the Jennings Patent 2,462,503 consist of a film base bearing a colloid (e. g. gelatin) silver halide emulsion layer, a stripping layer composed of a water-soluble macromolecular acetal of a hydroxyl polymer (e. g. polyvinyl alcohol) having a plurality of recurring intralinear

$$-CH_2-\underset{|}{C}HOH-$$

groups with an aldehyde containing a solubilizing group taken from the class consisting of hydrogen and a water-soluble salt-forming metal, which aldehyde is otherwise unsubstituted and a colloid (e. g. gelatin) silver halide emulsion layer.

In the device shown in Fig. 2 a water jet 13 impinges on the films at the point of separation of the films on the stripping roll 12.

In Fig. 3 the combined film after heating passes into a tank 14 which is filled with water to a level above the stripping roll 12.

The invention is, of course, not limited to a practicing of the invention in the apparatus schematically described above. It can be carried out in the apparatus described in Conklin U. S. application Ser. No. 777,472, now Patent No. 2,578,514, dated December 11, 1951, by placing an infra-red lamp or a series of infra-red lamps near the periphery of registration wheel 21 and between the registration rollers (viz., 30, 31 and 32) and the pin retracting roller (viz., 35) of the aforesaid apparatus. The film can otherwise be treated, transferred, stripped, processed, etc., as described in that application. However, efficient operation can be obtained with the Conklin apparatus modified by the addition of the infra-red heating means even when the stripping and transfer operation is carried out after exposure and prior to development.

The invention will be further illustrated but is not intended to be limited by the following examples.

EXAMPLE I

A photographic stripping film like that described in Example I of Jennings U. S. Patent 2,462,503 was exposed to a multicolor scene in combination with a green-blind, red-sensitive film as described in that patent. The bipack front film was then soaked for three minutes in a solution made by admixing the following constituents in the order named:

Citric acid, 40 grams
Water and sodium hydroxide to make 500 cc. of a pH 7 solution
Ethyl alcohol (95%) to make 1000 cc.
Formaldehyde (40% aqueous), 20 cc.

The solution was maintained at a temperature of about 70° F. during this period. The wet film was then rolled into registration contact with a gel blank film made by coating a thin cellulosic acetate film base with a solution containing 4.60% gelatin, 0.80% chrome alum (10% aqueous solution), 0.02% saponin and the remainder water. This solution, however, was adjusted to a pH of 4.7 with sulfuric acid before coating. The combined films having their respective gelatin surfaces in adhesive contact were then heated by passing them between two 375 watt infra-red lamps which were maintained a distance of 8" apart and disposed on opposite sides of the films so that the surfaces were about 4" away from each lamp. The combined films were then cooled to 72° F. in air and separated under water at 72° F. The emulsion transfer to the gel blank was uniform and there was firm anchorage between the two gelatin surfaces of the respective films. When similar films were treated in like manner without the heat treatment, the emulsion transfer was unreliable due to poor adherence of the emulsion layer to the gelatin surface of the blank film.

EXAMPLE II

An exposed bipack front film of the type described in Example I was developed for 15 minutes in the following developer solution:

Na_2SO_3 (anhydrous)	grams	90.0
N-methyl-p-aminophenol sulfuric acid salt	grams	0.8
Hydroquinone	do	1.0
Borax	do	3.0
KBr	do	0.1

Water to make 1.0 liter.

The developer solution was maintained at a temperature of 68° F. The developed film was then fixed for 15 minutes in a fixing solution made by admixing the following two solutions:

Solution A

$Na_2S_2O_3$, crystals	grams	240
Na_2SO_3, anhydrous	do	6
Water (125° F.)	cc	600

Solution B

Boric acid	grams	6
Acetic acid, 28%	cc	35
Potassium alum	grams	12
Water	cc	220

Solutions A and B when mixed form approximately 1 liter of fixing solution. The fixed film was washed for 20 minutes in water and dried. Then the film was soaked for 85 seconds in the following solution at a temperature of 68° F.:

Citric acid, USP	grams	16
Monosodium phosphate ($NaH_2PO_4.H_2O$)	grams	5
Phosphoric acid (85%)	cc	4
Sodium tetralin sulphonate	grams	25
Sodium dodecyl sulfate mixture [1]	do	25
Water to make 1 liter.		

[1] A mixture of sodium n-alkylsulfates of 10 to 18 carbon atoms predominating in sodium dodecyl sulfate.

and rolled into contact with a gel blank film. The combined films were heated after the manner described in Example I and separated under water maintained at 72° F. It was found that the emulsion transfer was superior to that obtained when no heating step was carried out after the films were pressed into registration contact.

EXAMPLE III

A perforated motion picture stripping film of the type described in Example I of Jennings U. S. Patent 2,462,503 was exposed in combination with a green-blind, red-sensitive photographic film to a multicolor scene as described in that patent. The front or stripping film of the bipack was given a flash exposure along the edge areas to obtain fogging of such areas. The front film was then processed to form black and white images as described in Example II above. The rear film of the bipack was given a normal negative photographic processing.

The dried front film was then passed through a tank containing the soaking solution (maintained at 72–73° F.) described in Example II at a speed of 40 feet per minute so that the film was immersed in the tank for a period of 60 seconds. The front stripping film was then pressed into registration contact with a gel blank film as described in Example I, heated and separated as described in that example. It was found that transfer around the edge was improved when the edge-fogged film was used as compared to a similar experiment wherein the film was not given a fogging exposure.

EXAMPLE IV

A nitrocellulose film base was provided with a thin gelatin coating to a weight of about 70 mg. per sq. dec. from the following aqueous solution:

	Percent
Gelatin	4.60
Saponin	0.02
Colloidal carbon (particle size 50 millimicrons)	0.20
Sulfuric acid to adjust to pH 4.7.	

The gel blank film thus produced had a coating with a density to visible light of 0.2 to 0.5.

An exposed bipack front stripping film of the type described in Example I above was processed in the same manner as described in Example III except that a registration sprocket was not used during the pressing of the film in registration contact. Instead, two interfitting pressure rollers were used. It was found that with a machine speed of 40 feet per minute and a distance of 8" between the pressure rollers and the stripping rollers that the emulsion transfer was only 50% complete when no heating was effected with the infrared lamp. However, when an infra-red lamp was placed between the pressure rollers and the stripping roller and disposed about 4" above the surface it was found that the transfer was 100% complete with excellent adherence between the gelatin surface of the silver halide emulsion and the gelatin surface of the gel blank.

EXAMPLE V

A bipack front stripping film like that described in Example I of Jennings U. S. Patent 2,462,503 was made as described in that patent except that the stripping layer contained dispersed prefogged silver bromide. This stripping layer was made in the following manner:

An o-sulfobenzaldehyde acetal of medium viscosity 100% hydrolyzed polyvinyl alcohol was prepared in anhydrous ethylene glycol with phosphoric acid as catalyst. Reaction occurred to the extent of inserting 5% of sulfonate sulfur of the total polymer weight. A solution prepared as follows from this polymer was coated between the emulsion layers at 85° F. and 25 feet per minute.

The above polymer in an amount of 168 grams was dissolved in 4872 cc. distilled water by heating at 140° F. for one hour. Eight cc. of 3 molar NaOH were then added. To 4500 grams of this polymer solution were added 350 grams of a 5% aqueous solution of low viscosity 100% hydrolyzed polyvinyl alcohol.

Distilled H_2O was added to make 8300 grams.
168 cc. .3M KBr solution were added.
175 cc. .3M $AgNO_3$ solution were added rapidly at 85° F.
pAg was adjusted to that of the adjacent silver iodobromide emulsion layers using .3M BRr solution.

The above mixture was stirred for ¼ hour at 110° F. with a white photoflood lamp 13" above the surface of the mixture. 160 cc. of 5% saponin solution were added. pH was finally adjusted to 7.0±.1 at 85° F. using 1N NaOH and 1.2N HCl.

The above front film was exposed to a scene in bipack combination with a rear film. The front film was processed as in Example II. On stripping the front film using the soaking solution described in Example II, gel blank, and infra-red heating as in Example II it was observed that stripping was easier (required less pulling) than for a control coating with no colloidal silver in the strip layer.

This processed film developed up a silver density of about 0.10 in the strip layer. This can easily be increased in order to obtain larger effects. When the films were stripped apart by bending the gel blank away from the stripping film, it was observed that the strip layer adhered almost completely to the transferred emulsion layer. The stripping layer with its colloidal silver was easily removed by water washing and gentle rubbing action.

The invention is, of course, not limited to the particular steps and apparatus described above. To the contrary the heating step may be combined with various other treating steps. It is especially useful in transfer and stripping operations of the kind described in Grumbine and Umberger, application Serial No. 27,608, filed May 17, 1948, now abandoned, and Grumbine and Umberger application Ser. No. 115,772, filed September 14, 1949, wherein the anchorage between the gelatin surfaces of the gel blank film and the gelatin-image bearing layer of the stripping film is improved by adding an anionic, water-soluble, surface-active wetting agent to the

aqueous transferring bath and adjusting the pH to 4.5 or below, e. g., 1.0 to 4.5. It is also useful with the films and in the processes disclosed in Umberger Serial No. 115,943, filed September 15, 1949, now U. S. Patent No. 2,612,446.

This invention has the advantage that it provides an improved method of transferring an image-bearing layer from a stripping film to a new support. Another advantage is that the invention provides an improved degree of adherence between the transferred image-bearing layer and the support. A further advantage is that the process can be carried out in conventional types of apparatus by the addition of readily available simple devices or articles, for instance, the common type of infra-red lamps.

A further advantage of a preferred aspect of the invention is that it provides improved and adequate adherence at the edges of perforated motion picture film.

A still further advantage is that stripping and transferring is made possible at higher speeds than can be achieved without infra-red heating.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. A process of transferring an image-bearing thermally-reversible colloid layer from a stripping film to another film base having a thin thermally-reversible colloid layer which comprises soaking said stripping film in an aqueous bath, pressing the wet colloid surface of the first-mentioned layer into registration contact with the colloid surface of the other film base, heating the adherent films with infra-red rays while they are in such contact and stripping the second film base with the adherent image bearing layer from the remainder of said stripping film.

2. A process of transferring a silver-image-bearing thermally reversible colloid layer from a stripping film to another film base having a thin thermally-reversible colloid layer which comprises soaking said stripping film in an aqueous bath, pressing the wet colloid surface of the first-mentioned layer into registration contact with the colloid surface of the other film base, heating the adherent films with infra-red rays while they are in such contact to blend the colloid layers and stripping the second film base with the adherent silver-image-bearing layer from the remainder of said stripping film while maintaining the film in an aqueous bath during the stripping operation.

3. A process of transferring an image-bearing gelatin layer from a stripping film to another film base having a thin gelatin layer which comprises soaking said stripping film in an aqueous bath, pressing the wet gelatin surface of the first-mentioned layer into registration contact with the gelatin surface of the other film base, heating the adherent films with infra-red rays to blend the gelatin layers and stripping the second film base with the adherent image-bearing layer from the remainder of said stripping film.

4. A process of transferring an image-bearing gelatin layer from a stripping film to another film base having a thin gelatin layer which comprises soaking said stripping film in an aqueous bath, pressing the wet gelatin surface of the first-mentioned layer into registration contact with the gelatin surface of the other film base, heating the adherent films with infra-red rays to blend the gelatin layers and stripping the second film base with the adherent image-bearing layer from the remainder of said stripping film while maintaining the film in an aqueous bath during the stripping operation.

5. A process of transferring an outer image-bearing gelatin layer, which is adhesively joined to layer on a perforated motion picture film base by means of a water-soluble macromolecular acetal of a hydroxyl polymer having a plurality of recurring intralinear

$$-CH_2-\underset{|}{C}HOH$$

groups with an aldehyde containing a solubilizing group taken from the class consisting of —COOZ and —SO_3Z where Z is a member taken from the group consisting of hydrogen and water-soluble salt-forming metal, which aldehyde is otherwise unsubstituted, to a perforated film bearing a gelatin layer, which comprises soaking the stripping film in an aqueous bath containing an acid and an anionic surface active wetting agent, pressing the gelatin surfaces of the respective films into registration contact, heating the combined films with infra-red rays so that the adherent layers blend at their surfaces, passing the combined film into an aqueous bath and stripping the second film with the adherent image-bearing layer from the stripping film.

6. A process of transferring an outer silver-image-bearing gelatin layer, which is adhesively joined to a layer on a perforated motion picture film base by means of a water-soluble macromolecular acetal of a hydroxyl polymer having a plurality of recurring intralinear

$$-CH_2-\underset{|}{C}HOH$$

groups with an aldehyde containing a solubilizing group taken from the class consisting of —COOZ and —SO_3Z where Z is a member taken from the group consisting of hydrogen and water-soluble salt-forming metal, which aldehyde is otherwise unsubstituted, to a perforated film bearing a gelatin layer, which comprises soaking the stripping film in an aqueous bath containing an acid and an anionic surface active wetting agent, pressing the gelatin surfaces of the respective films into registration contact, heating the combined films with infra-red rays so that the adherent gelatin layers blend at their surfaces passing the combined film into an aqueous bath and stripping the second film with the adherent image-bearing layer from the stripping film while the films are under water.

7. A process which comprises exposing to a multicolor scene a perforated motion picture stripping film having an outer light-sensitive gelatin silver halide emulsion layer releasably joined by means of a water-soluble adhesive to a layer on the film, giving the film a flash exposure to light along the perforated edges of the film, developing, fixing, washing and drying said film, soaking the processed film in an aqueous bath, pressing the web surface of said outer layer into registration contact with the gelatin surface of a similarly perforated blank film, heating the combined films with infrared rays to blend the adherent gelatin surfaces, and stripping the gelatin blank film with its adherent silver-image-bearing layer from the remainder of the stripping film.

8. A process of transferring an image-bearing gelatin layer from a stripping film to another film base having a thin gelatin layer which has inti-

mately dispersed therethrough colloidal particles of material strongly absorptive of infra-red rays which comprises soaking said stripping film in an aqueous bath, pressing the wet gelatin surface of the first-mentioned layer into registration contact with the gelatin surface of the other film base, heating the adherent films while in contact with infrared rays to blend the gelatin layers, and stripping the second film base with the adherent image-bearing layer from the remainder of said stripping film.

9. A process of transferring a silver-image-bearing gelatin layer from a stripping film having dispersed in the stripping layer thereof colloidal particles of material strongly absorptive of infrared radiations, to another film base having a thin gelatin layer which comprises soaking said stripping film in an aqueous bath, pressing the wet gelatin surface of said stripping film into registration contact with the gelatin surface of the other film base, heating the adherent films with infrared radiation to blend the gelatin layers and stripping the second film base with the adherent silver-image-bearing layer from the remainder of said stripping film.

10. A process which is set forth in claim 9 wherein the material absorptive of infrared rays is colloidal carbon.

JACOB QUENTIN UMBERGER.

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