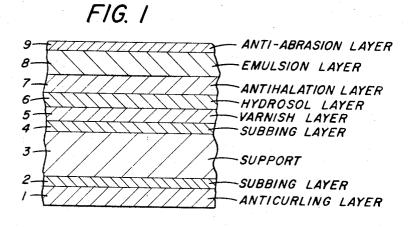
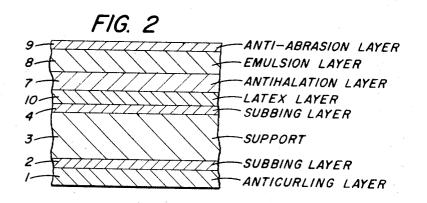
D. J. GALLOIS ET AL 3, LIGHT SENSITIVE ELEMENT FOR PREPARING ETCHING RESIST FOR GRAVURE PURPOSES Filed Feb. 21, 1968





D'ANIEL J. GALLOIS CLAUDE L. E. GUESTAUX MONIQUE L. LAUVERJAT INVENTORS

BY Hanny & Byers

ATTORNEY

**United States Patent Office** 

**1** 3,585,037

LIGHT SENSITIVE ELEMENT FOR PREPARING ETCHING RESIST FOR GRAVURE PURPOSES Daniel J. Gallois, Claude L. E. Guestaux, and Monique L. Lauverjat, Vincennes, France, assignors to Eastman Kodak Company, Rochester, N.Y. Filed Feb. 21, 1968, Ser. No. 707,131 Claims priority, application France, Nov. 13, 1967, 127,848 Int. Cl. G03c 1/90 U.S. Cl. 96-83 10 Claims

## ABSTRACT OF THE DISCLOSURE

Gravure resist film comprising resinous binding layers 15 which permit the stripping of the temporary support from the photosensitive emulsion, after wet transfer without the formation of blisters in the emulsion. The inclusion of compounds soluble in processing baths, such as hydroquinone, in a temporary binding varnish layer, and according to another modification, the inclusion of a water sensitive compound, such as casein, in a temporary binding latex layer, permits the simple removal of resinous material adhering to the photosensitive emulsion, after stripping, with  $35^{\circ}$  to  $40^{\circ}$  C. water. No organic solvent 25 is required for the removal of such residues from the emulsion.

This invention relates to light sensitive elements for use in preparing etching resists for gravure purposes. In one 30 embodiment, it concerns the incorporation in resinous binding layers of water soluble compounds.

In Guestaux et al. U.S. Pat. 3,396,025, issued Aug. 6, 1968, there is disclosed and claimed a photosensitive product which is useful in the preparation of a gravure resist and which comprises a temporary support of good dimensional stability which can be easily stripped generally without the aid of an organic solvent. The photosensitive product consists of a customary film support such as of cellulose acetate, polystyrene or polyethylene terephthalate overcoated with layers in the following order: (1) a subbing layer if desired, (2) a water impermeable layer comprising a polymer of a synthetic resin, this layer being coated from a solution (varnish) or from a suspension, (3) a stripping layer formed from a hydro- 45 sol of an acrylic copolymer as for example a mixture of gelatin with a copolymer of ethyl acrylate and acrylonitrile, (4) an antihalation layer composed of a gelatin layer containing a dye or Carey Lea silver, (5) an unhardened gelatin silver halide emulsion layer and pos- 50 sibly (6) an antiabrasion layer.

After exposure and tanning development, the product is applied onto the moist surface of a gravure cylinder. The emulsion layer is placed in contact with the cylinder. The film support is carefully stripped from the cylinder <sup>55</sup> permitting the emulsion to adhere to the cylinder following which the emulsion is washed in 35° to 50° C, water to remove the nontanned areas and to eliminate substances which might remain on the emulsion layer following the stripping. <sup>60</sup>

The light sensitive element described in the aforesaid application yields excellent results and constitutes an improvement over conventional light sensitive elements which elements required cold water to permit stripping of the film support and required special care to prevent 65 the formation of blisters on the emulsion layer. However, many of the synthetic resins employed in the layers of the light sensitive element of the aforesaid application require the use of an organic solvent to facilitate their removal after wet transfer and stripping of the support 70 from the emulsion layer. The use of water, alone, at a temperature of 38° to 50° C. is insufficient for the re-

moval of the resinous residue from the silver halide emulsion layer in many instances.

Novel light sensitive elements have now been discovered that comprise layers of synthetic resins that may be readily removed from the silver halide emulsion layer after wet transfer and stripping of the film support, by simple treatment with water, alone, at a temperature of  $35^{\circ}$  to  $40^{\circ}$  C. without the necessity for an organic solvent.

In accordance with this invention, a compound, such as hydroquinone, which is soluble in conventional processing baths is incorporated into the organic solution of the resin which is to constitute the temporary binding layer or varnish layer of the gravure transfer film. This modified varnish results in a resin layer which may be easily removed from the silver emulsion layer after wet transfer and stripping, merely by treatment with water at a temperature of  $35^{\circ}$  to  $40^{\circ}$  C.

The photosensitive product of this aspect of the invention thus comprises, broadly, a gravure resist film comprising a dimensionally stable, temporary, possible subbed film support containing thereon in the following order: (1) a temporary binding varnish layer composed of an organic solvent soluble synthetic resin and a compound soluble in processing baths, (2) a layer formed from 10 to 15 parts of gelatin and from 85 to 90 parts (dry weight) of a lower alkyl acrylate copolymer and containing a surface active agent, in which the alkyl acrylate moieties constitute from about 60% to about 90% of the whole weight of the polymer, hereafter called "hydrosol layer" (3) an antihalation layer, (4) a light sensitive gelatin silver halide photographic emulsion and if desired (5) an antiabrasion layer, all these gelatin containing layers being free from hardener agents.

Surprisingly, it has been found that by incorporating a compound that is soluble in the processing baths in the organic solvent solution of the polymer that is to constitute the temporary binding layer, i.e. the layer between the subbed support and the hydrosol layer, such polymer may be easily removed from the silver emulsion layer without the need for an organic solvent. The polymeric residue is easily removed by washing with  $35^{\circ}$  to  $40^{\circ}$  C. water. In addition, the temporary film support can be stripped from the emulsion layer without the formation of stripping blisters in the silver emulsion layer,

According to another aspect of this invention, the temporary binding layer may comprise a modified latex layer formed from an aqueous dispersion of a synthetic resin which is insoluble and dispersible in water and which contains a directly water soluble compound or a water soluble compound after processing in an alkaline bath, or a water swellable compound such as casein. Such a compound will be hereafter called "water sensitive compound." Such a layer will be hereafter called "latex layer." The inclusion of the water sensitive compound permits the removal of the latex layer from the photosensitive emulsion, after stripping of the temporary support, by merely treating with water at a temperature of  $35^{\circ}$  to  $40^{\circ}$  C.

The employment of the modified latex layer as a temporary binding layer has many additional advantages. For example, the modified latex layer may be employed as the sole resinous stripping layer between the support and the photosensitive emulsion and the hydrosol layer may be dispensed with, if desired. Also, the modified latex layer is applied from an aqueous suspension of a polymer of a synthetic resin rather than from an organic solution, as is the case of the temporary binding layer previously described. This method of application gives added safety to the manufacturing operation, since it avoids the use of solvents that are volatile and inflammable.

The film of the modified latex aspect of the invention comprises, broadly, a dimensionally stable, temporary, possibly subbed film support containing thereon in the following order: (1) a temporary binding layer formed from a latex of a synthetic resin which contains a water 5 sensitive compound, (2) an antihalation layer, (3) a light sensitive gelatin silver halide photographic emulsion and if desired (4) an antiabrasion layer, all these gelatin containing layers being free from hardener agents.

The film support (possibly subbed) of this modification 10 may be easily stripped from the latex coating without the formation of blisters in the emulsion layer, and residues of the modified latex layer may be easily removed from the emulsion by contact with water at a temperature of from 35° to 40° C.

In the attached illustrative drawing;

FIG. 1 represents a greatly enlarged cross section of a product in accordance with a preferred embodiment of the invention.

FIG. 2 represents in similar fashion a cross section of 20 a photographic product according to a preferred modification of the invention.

FIG. 1 illustrates a product comprising an anticurling layer backing 1 and a subbing layer 2 for the support 3which carries successively and in a superimposed rela- 25 incorporating a water sensitive compound in an aqueous tionship a subbing layer 4 a varnish layer 5, a hydrosol layer 6, an antihalation layer 7, a silver emulsion layer 8 and an antiabarasion layer 9.

FIG. 2 illustrates a photographic product of the modified structure of this invention in that the latex layer  $10^{-30}$ containing a water sensitive compound is placed between the subbing layer 4 and the antihalation layer 7.

The thickness of the layers represented in FIGS. 1 and 2 are not intended to represent the exact scale. For example, the support may have a thickness of about 100  $^{35}$ microns, the antihalation layer a thickness of about 5 microns, the emulsion layer a thickness of about 15 to 20 microns, the antiabrasion layer and the subbing layers a thickness of about one micron and the varnish layer 5, synthetic resin layer 6 and latex layer 10, a thickness of 2 40to 5 microns. It is apparent that some latitude should be allowed in the compounding of these various layers to form the products described.

As previously mentioned, the modified varnish layer 5 of FIG. 1 is produced by incorporating compounds 45 which are soluble in the processing baths, in an organic solution of the polymer which is to constitute the binding layer. Such compounds include hydroquinone, acrylamide, etc.

Organic solvent soluble synthetic resins which are suit- 50 able for employment in the varnish layer include polyisobutyl methacrylate, polyvinyl butyral, polyvinyl chlorideacetate, polycondensation products of bisphenol and maleic or fumaric anhydride, polyvinylidene chloride and acrylonitrile copolymers and the like. 55

The amount of the soluble compound, e.g. hydroquinone, that is employed in the varnish layer may vary over a wide range. Good results are obtainable with the soluble compounds in amounts of between about 20 and about 200% by weight of the organic solvent soluble polymer. 60

The hydrosol layer 6 of FIG. 1 may comprise a mixture of gelatin and a surfactant-containing lower alkyl acrylate copolymer hydrosol such as that contained in the product of French Pat. No. 1,282,219, the disclosure of which is hereby incorporated by reference. Thus, the  $\,^{65}$ polymer of the hydrosol may comprise the product resulting from the emulsion polymerization of a mixture of 60 to 90% ethylacrylate and 40 to 10% acrylonitrile.

The composition of the hydrosol layer may vary in the 70ratio of copolymer to gelatin between 90:10 and 85:15, based on solids weight, preferably being approximately 87:13. The dry coverage of this layer may be from 0.1 to 1.0 gram of solids per square foot with the preferred level at 0.3 to 0.4 gram per square foot.

This composition also contains a surfactant present as a result of the emulsion polymerization to prepare the hydrosol. The surface active agent is an anionic wetting agent having a long hydrophobic chain such as alkyl or aralkyl, etc. terminating in a sulfate or sulfonate group and optionally having intermediate polyethoxy, amide or other hydrophilic groups, such as:

1) The sodium salt of N-methyl-N-oleyl taurine,

- (2) Tetrasodium-N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate,
- (3) The sodium salt of a p-tertiary-octylphenoxy polyethoxyethyl sulfate where the number of ethoxy groups may average 3, but is usually a mixture of several chain lengths of different numbers of ethoxy groups, <sup>15</sup> (4) Sodium lauryl sulfate.

Instead of or in addition to the above, a cationic surface active agent useful for facilitating stripping is dioctadecyldimethyl-ammonium chloride, especially of commercial or technical grade.

The working limits of the surface active agent is from 1 to 5% by weight of the dry monomeric material in the preparation of the hydrosols, preferably from 2 to 4%.

The modified latex layer 10 of FIG. 2 is produced by dispersion of a synthetic resin such as styrene-butadiene resins, vinylidene chloride-acrylonitrile and ethyl acrylateacrylonitrile copolymers; modified polyvinyl chloride, the terpolymers of methyl methacrylate, vinyl chloride and vinyl isobutyl ether; polyacrylonitrile, styrene polymers plasticized with butyl phthalate, and the like.

The inclusion of a water sensitive compound modifies the properties of the latex so that the film is readily strippable and the latex layer may be easily removed from the silver emulsion by treatment with water at a temperature of 35° to 40° C. Such water sensitive compounds include casein, polymeric materials, such as terpolymers comprising butyl acrylate, styrene and methacrylamide, copolymers comprising vinyl acetate, or compounds such as hydroquinone, acrylamide, or compounds which are water soluble after treatment in alkaline baths, such as cellulose acetate phthalate, etc. Suitable amounts of the water sensitive compounds include from about 2 to about 100% by weight of the solid portion of the latex.

The incorporation of casein into the aqueous polymeric dispersion, which constitutes a preferred embodiment, renders the resulting latex layer porous upon wet transfer of the film to the copper cylinder. The latex residue that remains after stripping may be easily removed from the silver emulsion layer with water at 35° to 40° C. The principal reason for incorporating the casein into the latex layer is to avoid the undesirable anchoring of the latex layer to the photosensitive emulsion layer and to the metal parts of the coating apparatus and to permit its easy removal with warm water. However, the presence of casein in the latex layer additionally increases the ease of stripping the temporary support from the photosensitive emulsion.

The stripping readiness of the casein containing latex coating may be further enhanced by incorporating therein a polymer which is both saponifiable, and compatible with the latex. Such polymeric materials include cellulose acetophthalate, copolymers of vinylmethylether and maleic anhydride, modified esters of pentaerythrite and colophony, copolymers of styrene and maleic anhydride, and the like. Generally, the saponifiable polymers may be employed in amounts of from about 2 to about 50% by weight of the solid portion of the latex.

The support for the photosensitive product may be any film support customarily used which has good dimensional stability, such as cellulose acetate, cellulose acetate butyrate, polystyrene, poly(ethylene glycol terephthalate) and the like, wherein the thickness usually runs from 75 0.065 to 0.325 mm. In case of polyester supports even 5

thinner sheets may be used. Before applying the various layers to a support, it may be desirable to treat the surface of the support with trichloroacetic acid prior to coating with the various layers which facilitates the adherence of the layers thereto. The polyester support layer may, if desired, have a subbing layer such as a terpolymer of vinylidene chloride, methyl acrylate and itaconic acid, such as disclosed in U.S. Pat. 3,282,643, cellulose nitrate, etc. This subbing layer overcoated with a thin layer of gelatin is preferred. 10

The antihalation layer comprises a layer of gelatin containing an antihalation dye, such as a yellow Carey Lea silver colloidal dispersion or a manganese dioxide dispersion. The use of a yellow Carey Lea silver dispersion is preferred at the coverage of 0.7 to 0.8 gram per square 15foot, dry weight.

However, some antihalation dyes which may be used in lieu thereof in the antihalation layer include:

- (1) Congo red,
- (2) The product which results when 2-naphthylamine- 20 6,8-disulfonic acid is diazotized and coupled with an equimolar amount of chromotopic acid,
- (3) The product (Schultz No. 208) which results when 1-naphthylamine-4-sulfonic acid is diazotized and coupled with an equimolar amount of 1-naphthol-4-sulfonic 25 acid.

The emulsion layer comprises a light sensitive silver halide gelatin emulsion with the gelatin of this layer being unhardened and without any hardeners therein. A silver 30 bromoiodide emulsion has been found to be quite suitable for this purpose. However, various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide. The reason for the emulsion layer 35 being in unhardened condition is that in use of the element the gelatin of the silver halide emulsion layer is differentially hardened in the processing bath so that a tanned image is formed in the emulsion layer. Hardening of the gelatin in the emulsion layer would interfere with 40 the use of the element in accordance with the invention.

The antiabrasion layer that may be employed for the protection of the photosensitive emulsion layer may be of an usual type. A suitable antiabrasion layer is made from a mixture containing, for example, 22 parts of starch and 100 parts of gelatin. Such an antiabrasion layer is applied at a gelatin coverage of 93 mg. per square foot.

An anticurl layer may be utilized as a backing for the photosensitive element of this invention, and such layer may be of a composition similar to the antihalation layer 50described above. This layer prevents the curling of the support due to the photosensitive emulsion on the opposite side thereof. For example, the anticurl layer may be a conventional gelatin pelloid containing either dyes or manganese dioxide. Other suitable anticurl layers include 55a nitrocellulose lacquer, an alkyd resin coating or a lacquer including both nitrocellulose and alkyd resin. These coatings may be applied from a suitable solvent. Other suitable anticurl layers include an unhardened gelatin layer (thus avoiding the contamination of emulsion layers) 60 containing a compound capable of oxidizing the hardening developer used in the developing step (for example, pyrogallol), said compound being such as, for example, cupric ferrocyanide, mercuric iodide, lead iodate, methylene blue, etc. 65

The anticurl layer is preferably of the same thickness as the light sensitive emulsion layer.

The various layers forming the photosensitive element of this invention including the varnish layer may be applied to the support which has a subbing layer, covered 70with a thin layer of gelatin, by one of the well known techniques such as hopper, scraper, bead coating, transfer by immersed rollers or any of the other procedures well known in the art for the application of layers in preparing photographic products. Upon drying of the varnish 75layer, the hydrosol and antihalation layers are coated,

simultaneously, upon the varnish layer by one of the aforesaid methods. The silver emulsion layer and the antiabrasion layer are applied over the antihalation layer in a separate run. The layers are applied in the order mentioned.

The same general procedure is employed in producing the resist film of this invention which includes the latex layer that contains a water sensitive compound. The latex layer is applied to a subbed support simultaneously with a layer of unhardened gelatin which may contain an anti-

halation dye. Then, in a subsequent run the silver emulsion and antiabrasive layer are simultaneously coated onto the antihalation layer. The various layers are applied in the order mentioned.

The film of this invention may be used in any of several gravure processes. For example, the element in accordance with the invention may be subjected to short exposure while in effective contact with an image or any other type of element, such as the image modulated light beam from a photoelectric scanning device which will impart a latent image to the silver halide emulsion, as is well known in the photographic art.

After exposure, the element, the emulsion of which has been exposed, is developed, fixed, washed and dried, which procedure differentially affects the gelatin of the emulsion layer imparting a hardening and insolubilizing effect to the gelatin around the silver grains of the image.

A suitable method for processing the film is by a series of steps as follows:

(1) The element is bathed at 68° F. for 2 minutes in a developing solution consisting of:

Gra	ms
Elon	1.0
Hydroquinone	2.0
Pyrogallic acid	6.0
Sodium sulfite	
Potassium bromide	
Sodium sulfate7	
Potassium metabisulfite	5.0
Water to make 1 liter.	

(2) The liquid is drained off for 15 seconds.

- (3) The element is developed at 68° F. for 2 minutes in an alkaline solution consisting of:
- Trisodium phosphate \_\_\_\_\_grams\_\_\_ 100 45Sodium sulfate \_\_ -----do\_\_\_\_ 75 Phosphoric acid (85%) \_\_\_\_\_cc\_\_ 5 Water to make 1 liter.

(4) The liquid is drained off for 15 seconds and rinsed for 60 seconds at 68° F. in a bath consisting of sodium diacetate 100 grams, water to make 1 liter.

(5) Fixing is carried out for 5 minutes at 68° F. in a bath of the following compositions:

5	Sodium thiosulfategrams	240
-	Sodium sulfite (desiccated)do	10
	Sodium bisulfitedo	
	Glacial acetic acidcc	20
	Water to make 1 liter.	

(6) Wash in running water for 5-10 minutes. (7) Immerse in the following solution for 60 seconds

at room temperature:

Wetting agent (Kodak Photo-Flo)cc	10
Semicarbazide hydrochloridegram	1
Ammonium hydroxide (28%)cc	
Water to make 1 liter.	

or in a solution containing 2 to 4% glycerol in water,

(8) Excess liquid is removed and the film is dried at either room temperature or elevated temperature (below 30° C.).

After exposure and development, the film is applied to the moist surface of a gravure cylinder with the emulsion surface (or the antiabrasion layer if one is employed) being in contact with the copper cylinder. Following the

60

stripping of the support from the photosensitive layer, the nontanned gelatin along with any resinous material which is a residue of the resinous binding layers is easily removed by merely treating with water at 35° to 40° C.

The formation of the etched surface on the copper cylinder may be accomplished in any conventional manner. For example, the copper cylinder containing the relief image may be etched as follows: some sort of protection such as asphaltum may be applied to the areas of the copper which are unprotected by the image and 10are not to be etched. The copper may be then subjected to an etching operation such, for example, as with ferric chloride. The copper surface is thereby differentially etched inversely to the thickness and hardness of the gelatin which resides on the surface of the copper. There 15results relief images adapted for use in photogravure printing operations.

The invention will be illustrated by the following examples, but it is to be understood that the invention is not restricted thereto. The percentages are by weight unless 20 otherwise specified.

### **EXAMPLE 1**

Thirty grams of a resin comprising polyvinyl acetate chloride modified by treating with maleic acid are dis-25solved in a solvent composed of 940 grams of acetone. To the varnish solution is added 20 grams of hydroquinone. This solution is then coated onto an Estar [trademark for poly(ethylene glycol terephthalate)] support of 0.10 mm. thickness having a subbing layer composed of a terpolymer comprising 83% by weight vinylidene chloride, 15% by weight methylene acrylate and 2% by weight itaconic acid. The coating has a thickness of 2 to 3 microns upon drying. Gelatin is applied over this layer in an amount of 40 mg. per square decimeter resulting in a gelatin layer having a thickness after drying of  $^{35}$ approximately 5 microns.

Next, there is applied, in succession, a layer of a hydrosol comprising a dispersion of 453 grams of gelatin in 7200 grams of a latex having about 40% solids content 40and comprising a copolymer of ethyl acrylate and acrylonitrile, an antihalation layer of gelatin containing a Carey Lea silver dispersion, a gelatin silver halide emulsion layer and an antiabrasion layer. The dry thickness of the hydrosol coating is 2 to 3 microns.

The resulting film is then submitted to the operations 45 of exposure, hardening development and transfer onto a wet copper cylinder. In order to evaluate the qualities of the resulting material, the stripping force of a one centimeter wide bit of the unexposed and dry material and of the material developed at the time of stripping after 50wet transfer emulsion side onto the copper cylinder are measured with a dynamometer at an angle of 45°. The presence or absence of blisters resulting from stripping on the emulsion is also evaluated by a practical test on a larger sheet of film. 55

The stripping force of the dry unexposed material and of the material developed at the time of stripping, i.e. after wet transfer is about 200 grams and 25 grams respectively. No formation of blisters is observed after the support has been stripped off.

After stripping the support from the element on the cylinder, the nontanned gelatin of the emulsion layer is removed by washing with water at a temperature of 35° to 40° C. The residues of the varnish and polymer layers are simultaneously removed by this simple water wash 65 treatment. The gravure cylinder is now ready for etching.

### **EXAMPLE 2**

Forty grams of polyvinyl acetate chloride modified by treating with maleic acid are dissolved in a solvent com- 70 posed of 920 grams of acetone. In addition, 40 grams of acrylamide are added to the solution. The solution is then coated onto a subbed Estar film base to give a coating having a thickness of 3 to 4 microns upon drying. The hydrosol layer, antihalation layer, gelatin silver 75 moved by means of water at a temperature of 40° C.

halide emulsion layer and antiabrasion layer are applied in succession as in Example 1. The resultant product is then applied to a copper cylinder in the same manner as described in Example 1.

The dry stripping forces and those after wet transfer are determined and found to be about 100 grams and 25 grams respectively. No blisters are noticeable on the silver emulsion after stripping, The removal of the varnish and resin layers from the emulsion layer is easily effected by spraying with water at a temperature of 35° to 40° Č

The following examples illustrate the aspect of this invention in which a water sensitive compound is incorporated into a latex layer, which constitutes the temporary binding layer, so that the varnish layer and the hydrosol layer may, in some instances, be replaced with a latex laver.

### EXAMPLE 3

Five hundred grams of an anionic aqueous dispersion having a pH of 7.5 and composed of a styrene polymer plasticized with butyl phthalate and which is comprised of 47% by weight dry material are mixed with 495 grams of water. The aqueous dispersion is commercially available under the trade name "Vinacryl 4000" from Vinyl Products Ltd. Five grams of casein are added to the latex.

Thereafter, the modified later layer is applied to a subbed Estar support and an antihalation layer of gelatin containing Carey Lea silver dispersion, a gelatin silver halide emulsion layer and an antiabrasion layer are successively coated onto the modified latex layer in the manner of Example 1. The product is then applied to a copper cylinder in the manner described previously, and the film support is stripped from the emulsion layer upon the copper cylinder.

The dry stripping forces and those upon wet transfer are about 50 grams and about 10 grams respectively. No blisters are formed on the emulsion after stripping. The modified latex coating is easily removed from the emulsion by merely sprinkling with water at a temperature of 40° C.

## **EXAMPLE 4**

For comparative purposes, the procedure of Example 3 is repeated, however, the amount of casein employed in the latex layer is increased to 37.5 grams.

As with the film of the previous example, no blisters are observed on the emulsion after the temporary support is stripped, and the latex coating is easily removed by contact with water at a temperature of 40° C. Accordingly, it is seen that the percentage of the water sensitive casein may be varied over a fairly wide range with equally good results obtainable.

The following examples illustrate the increased ease of stripping with a latex layer by the incorporation of a polymer that is saponifiable and compatible with the latex.

## **EXAMPLE 5**

Five hundred grams of Vinacryl 4000 and 7.5 grams of casein are mixed with 487.5 grams of water. Additionally, 5 grams of cellulose acetophthalate, a saponifiable polymer containing 25% by weight phthaloyl are incorporated into the mixture. The resulting latex layer is coated onto a subbed support and formed into a film as in the previous examples. The resulting film is exposed and applied to a copper cylinder by wet transfer of the emulsion side onto the cylinder.

The dry adhesive forces and those upon wet transfer are 6 grams in each case. No stripping blisters are formed on the emulsion and the latex coating is very easily re10

# **EXAMPLE 6**

The procedure of Example 5 is repeated, but the amount of cellulose acetophthalate is increased to 25 grams.

The dry and wet stripping forces are identical with those obtained in Example 5. Likewise, no blisters are formed on the emulsion upon stripping. Here again, 40° C. water easily removes the latex coating.

### **EXAMPLE** 7

The procedure of Example 5 is repeated, however, a copolymer composed of vinylmethylether and maleic anhydride, a modified ester of pentaerythrite and colophony, and a copolymer of styrene and maleic anhydride which are saponifiable polymers compatible with the latex, are 15 substituted for cellulose acetophthalate.

The temporary support of each of the resultant films strips easily, no stripping blisters are formed on the emulsion and the latex is easily removed by water at a tem- $\mathbf{20}$ perature of 40° C. in each case.

The following examples further illustrate the advantages realized by incorporating a water sensitive polymer into the latex layer.

### **EXAMPLE 8**

Using the same procedure as before, a subbed Estar film base is coated with an aqueous dispersion comprising 250 grams of a copolymer of styrene and butadiene in a dispersion comprising 47% by weight solids, 500 grams of a terpolymer composed of butyl acrylate, styrene and methacrylamide as an aqueous dispersion composed of 25% by weight solids and 250 grams of water. The dry adhesion forces and those upon wet transfer are 150 grams and 10 to 20 grams, respectively. No stripping blisters are formed on the emulsion and the latex coating 35 is easily removed by washing with water at a temperature of 40° C.

#### **EXAMPLE 9**

The procedure of Example 8 is repeated employing an 40 aqueous dispersion containing 500 grams of Vinacryl 4000, 250 grams of a vinyl acetate copolymer, 7.5 grams of casein and 252.5 grams of water.

The dry stripping forces and those upon wet transfer are about 50 grams and about 10 grams, respectively. As 45 expected, no stripping blisters are formed on the emulsion. The latex layer is easily removed from the emulsion by merely washing with water at a temperature of 40° C.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will 50 be understood that variations and modifications can be effected within the spirit and scope of the invention as

10

described hereinabove and as defined in the appended claims.

We claim:

1. A gravure resist film comprising dimensionally stable, 5 temporary, film support containing thereon

- (1) a varnish layer composed of an organic solvent soluble synthetic resin and about 20 to about 200 percent by weight of said resin of a compound soluble in aqueous photographic processing baths,
- (2) a layer composed of 10 to 15 parts of gelatin and 85 to 90 parts (dry weight) of a surfactant-containing lower alkyl acrylate copolymer latex in which alkyl acrylate units comprise 60 to 90 weight percent of the total polymer,
- (3) an antihalation layer and
- (4) a hardener-free light sensitive gelatin silver halide photographic emulsion layer, all in that order.

2. The film of claim 1 wherein the film support is subbed.

3. The film of claim 1 wherein the said emulsion layer has thereon an antiabrasion layer.

4. The film of claim 1 wherein the compound soluble in processing baths is hydroquinone.

5. The film of claim 1 wherein the compound soluble 25 in processing baths is acrylamide.

6. The film of claim 1 wherein the varnish layer comprises maleic acid modified polyvinylacetate chloride and hvdroquinone.

7. The film of claim 1 wherein the said acrylate copolymer comprises a copolymer of ethyl acrylate and 30acrylonitrile.

8. The film of claim 1 wherein said surfactant is an anionic wetting agent.

9. The film of claim 1 wherein said compound soluble in processing baths is cellulose acetate phthalate.

10. The film of claim 1 wherein said antihalation layer contains Carey Lea silver.

### References Cited

## UNITED STATES PATENTS

3,148,063 3,369,903	9/1964 2/1968	Yackel et al 96—83 Harvey 96—83				
FOREIGN PATENTS						
1,282,219	8/1965	France 96-83				

RONALD H. SMITH, Primary Examiner

U.S. Cl. X.R.

96-84R, 87R