Aug. 17, 1965 G. M. CORYELL ET AL 3,201,250

DIMENSIONALLY STABLE GELATIN-CONTAINING FILM PRODUCT

Filed Jan. 12, 1959

Fig. 1

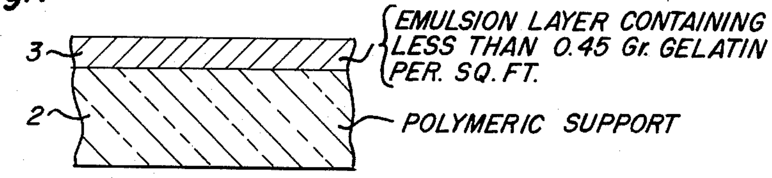
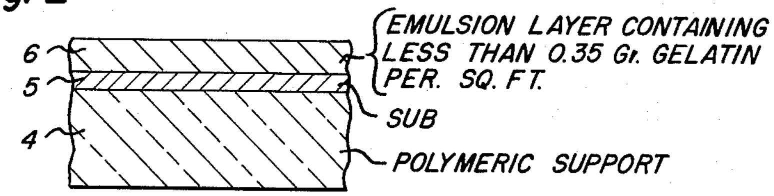


Fig. 2



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DIMENSIONALLY STABLE GELATIN-CONTAINING FILM PRODUCT

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This invention concerns the preparation of a composite type film product that is relatively dimensionally stable. More particularly, this invention concerns a photographic film product made up of a subbed stable film base, which film base carries a relatively dimensionally stable gelatin-containing emulsion layer.

It is well known that the older types of photographic film products were susceptible of dimensional change when subjected to varying temperature or humidity and the like conditions. That is, the film product may increase or decrease somewhat in length or width or otherwise dimensionally change under different conditions of humidity or comparable treatment. Under conditions of practical operation where film products are passed through various processing baths or in use or storage may encounter elevated temperatures, dimensional changes such as occurred in the older type products may be rather substantial. As has already been discussed, the prior art products which are subjected to such type of change may not be particularly suitable for precision work and for various other uses.

With the availability of more stable film base material such as sheeting made from polystyrene and polyesters as well as certain other polymeric type of sheeting, it has been proposed to use such more stable sheeting as the base in photographic products. While such use of this more stable base material has improved dimensional stability to some extent there still exists problems and certain new problems have been introduced. For example, there is now some problem in how to suitably obtain adhesion of layers to polyester sheeting inasmuch as such polymer type of sheeting in many instances is not particularly receptive to lamination or the formation of composite products therefrom. Also, even when the adhesion of standard emulsion compositions to such polymeric film base is successful, the value of the increased stability of such bases is largely overshadowed inasmuch as the layers affixed thereto are frequently dimensionally unstable to a substantial extent. It has been proposed to use a polymeric vehicle in place of the usual emulsion vehicles to obtain dimensional stability. That has merit but in certain instances it is still desired in the industry to have a gelatin-type emulsion.

It is, therefore, believed apparent that the development of a composite film product which overall is relatively dimensionally stable but which to some extent resembles the older type of film products represents a highly desirable result. After extended investigation we have found what we believe to constitute an improved photographic film product in that its overall dimensional stability is very good and with respect to which the emulsion layer generally possesses properties somewhat comparable to the properties of the older type of film products, yet the emulsion layer of the present invention is relatively dimensionally stable.

This invention has for an object to provide a composite

photographic film product which has overall improved dimensional stability and yet in some of its other properties is similar to the older type film products. Another object is to provide a film product which contains in its makeup certain polymeric film base materials in combination with a certain type emulsion layer. Still another object is to provide a film product of the class indicated wherein the emulsion layer exhibits good dimensional stability in combination with certain supporting bases. Still a further object is to provide a film product which may contain certain special subs or comparable treatment whereby any tendency of the film product to separate into layers is minimized. Other objects will appear hereinafter.

In the broader aspects of our invention we have found it is possible to improve the dimensional stability of photographic film products, particularly products to be used for graphic art purposes. In films of this type, especially when used in the making of color reproductions, dimensional stability is of prime importance because of the registration problems involved. In work with the new more stable film bases, we discovered that a limiting factor appears to be the amount of gelatin used in the emulsion and the amount of gelatin pelloid coated on the back of the support. We have found that maximum dimensional stability can be obtained only if the amount of gelatin per unit area is reduced to a lower value than that normally used in films of this type. The improvement which can be obtained in dimensional stability when low gel emulsions are used is believed to be of practical significance.

In further detail, we have found that for an overall dimensionally stable light-sensitive film product wherein the emulsion layer contains gelatin that the gelatin content should be below about 0.45 gram per sq. ft. of film area. By employing a gelatin-containing emulsion we obtain a product which somewhat resembles the older type film products in certain properties. However, by keeping the gelatin content below the aforementioned value of 0.45 gram per sq. ft. we have found that the dimensional stability of the film product is materially improved.

The layer of the present invention which contains gelatin of less than 0.45 gram per sq. ft., may be applied to various film supports. Although the film product may be made with a triacetate support, we prefer to employ a polymeric support such as polystyrene or polyester film base. Such polymeric film support may be of .004–.008 inch thickness and is preferred because of its dimensional stability. Suitable polystyrene support material is described in companion Patent 2,816,027 from the same laboratories as the present invention. Such polystyrene support material may be used as described in this patent but preferably it would be treated as will be described below.

Suitable polyester support material is described in U.S. Patent 2,627,088. The polyester support may be produced in accordance with this patent wherein certain layers are applied during the manufacture of the support. However, we may obtain the polyester support and then separately sub it or otherwise treat it as will be described below. When using polymeric base material, in order to obtain good adhesion of the emulsion layer to the base material, it is generally desirable that the polymeric base material be treated in some manner for facilitating the adhesion of the layers applied to the base.

Polyester base probably presents more difficulties of securing the adhesion of added layers thereto than other type of bases. However, such polyester base material can be rendered receptive to further layers, such as the special emulsion layer of the present invention, by various treatments illustrated by treatment with a discharge from a Tesla coil, certain solvents, and subbing. The following will illustrate several ways in which polyester base material may be treated for rendering it receptive to further layers.

Fully processed polyethylene terephthalate support can be satisfactorily subbed for gelatin photographic emulsions by the following procedure: (1) The base is treated with a solution of a terpolymer, e.g. $R_aV_{cl}C$[1], in a suitable solvent and the terpolymer layer dried. (2) The terpolymer is overcoated with a cellulose nitrate solution in attack solvents for the terpolymer and dried. (3) The cellulose nitrate layer is overcoated with a gelatin or gelatin+cellulose nitrate solution in attack solvents and dried.

A typical example is described. A 1.5 percent solution of $R_aV_{cl}C$ is made in redistilled tetrahydrofuran. RF-M[2] base is coated with this solution using a whirling vacuum coating block, the block being at about 60° C. The coated layer is dried at 60° C. for 3 minutes. This layer is then overcoated at room temperature with a cellulose nitrate solution in attack solvents and dried for 3 minutes at room temperature. This layer is then overcoated with a regular gelatin sub and dried at room temperature. When overcoated with a gelatin emulsion and dried, the following typical adhesion results were obtained:

Base	Type Subbing	Terpolymer	Dry Adhesion (Peelback at 15% R.H.)	Wet Adhesion After Processing
RF-M[1]	3 step as described.	R_aV_{cl}	0.05-0.07″	0-0+

[1] RF-M=polyester base sold by E. I. du Pont de Nemours & Co.
0=excellent adhesion.
0+=very good adhesion but slightly poorer than 0.

Other solvents may be used such as cyclohexanone.

The pretreatment of the polyester base with the discharge from a Tesla coil before applying the terpolymer by the procedure just set forth above improves the dry adhesion of the unprocessed film. Wet adhesion is satisfactory initially except for some slight peelback from a cut edge. Dry adhesion after processing is not improved.

A typical example is described below.

EXAMPLE A

Fully processed polyethylene terephthalate base designated RF-M was placed on an aluminum plate and irradiated from the top by the discharge of a Tesla coil. This treated base was then subbed on the same side by the three step terpolymer process described above. Improvement in dry adhesion of the emulsion was obtained as shown in the following table:

Base	Type Subbing	Dry Adhesion Peelback		Wet Adhesion		Peeling of Wet Emulsion from Cut Edge	Dry Adhesion After Processing	
		15% R.H.	50% R.H.	1 Day	6 Wks.		15% R.H.	50% R.H.
RF-M	3 step process	C	D	A	A	Yes	C	Peeled.
RF-M	Tesla coil pretreatment plus 3 step process.	C	B	A	E	Yes	D	Peeled.

EXAMPLE B

Two additional runs were carried out. In one, the base was Tesla coil treated and then subbed on the opposite side. In the second run, the subbing was done on the treated side as in Example A. The data obtained are given in the following table:

Base	Type Subbing	Dry Adhesion Peelback		Wet Adhesion		Peeling of Wet Emulsion from Cut Edge	Dry Adhesion After Processing	
		15% R.H.	50% R.H.	1 Day	6 Wks.		15% R.H.	50% R.H.
RF-M	3 step process	C-	C-D	A	A-D	Yes	Peeled	Peeled.
RF-M	Tesla coil treated and then subbed on opposite side.	B-	C	A	D	Yes	C	D.
RF-M	Tesla coil and subbed on same side with 3 step process.	B	C	A	E	Yes	C	D.

The various letter ratings C, D, etc. in the above tables mean—

Dry Adhesion:

A. No failure (no feathering or peelback) excellent adhesion.
B. 0.02–0.05 inch peelback at 15% R.H., 0.05–0.15 inch peelback at 50% R.H. Very good adhesion.
C. 0.05–0.1 inch peelback at 15% R.H., 0.2–0.5 inch peelback at 50% R.H. Good adhesion.
D. 0.1 inch peelback at 15% R.H.. Nearly peels at 50% R.H. Doubtful passable adhesion.
E. Peels at 15% R.H. Poor adhesion.
F. Dry strips at 15% R.H. (failure). Very poor adhesion.

Wet adhesion—15 min. water wash (25° C.) after processing:

A. No failure. Excellent adhesion.
B. Scratched (fingernail scratch test) to the base but no rub off. Very good adhesion.
C. Trace of rub off. Fair adhesion.
D. Considerable ruboff. Poor adhesion.
E. All rubs off. Very poor adhesion.
F. Wet strips failure. Extremely poor adhesion.

Adhesion of processed emulsion, including peelback from a cut edge, can be improved by treatment of polyester base with either dichloro or trichloroacetic acid in a suitable solvent before or during the application of the terpolymer by the procedure described above.

Certain examples and comparison adhesion data are set forth below.

EXAMPLE C

Fully processed polyethylene terephthalate base designated as RF-M, was subbed with a 1.3 parts by weight of the $R_aV_{cl}C$ polymer (n-hexylacrylate, vinyl chloride,

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[1] C=Acrylic acid, R_a=n-hexylacrylate, V_{cl}=vinylchloride.

[2] RF-M=polyester base sold by E. I. du Pont de Nemours & Co.

acrylic acid) was dissolved in a mixture of 85 parts tetera hydrofuran and 15 parts of dichloroacetic acid, dried, overcoated with a cellulose nitrate solution containing attack solvents for the terpolymer, dried, overcoated with a gel sub, dried and finally overcoated with a gelatin emulsion which was slow dried. Adhesion data were also obtained with emulsion coatings on RF–M base, (1) subbed only by the 3 step process described above.

Marked improvement in dry adhesion was obtained with the emulsion on RF–M subbed by the 3 step process but with dichloroacetic in the terpolymer coating solution. Typical data are shown in the following table:

Base	Type Subbing	Dry Adhesion Before Processing, Peelback at—		Wet Adhesion After Processing	
		15% R.H.	50% R.H.	After 1 Day	After 6 Weeks
RF-M	3 step process	.15″	.57″	A[1]	A
RF-M	DCA in terpolymer	.00	.06	A	A-

[1] A is equivalent to 0^+, used above for rating preceding examples.

However, by this procedure, considerable DCA is left in the terpolymer layer. The dry adhesion test referred to above involves the use of the "Elmendorf Tear Tester." Information concerning this type test is provided in:

(a) "Standard Method of Test for Internal Tearing Resistance of paper," A.S.T.M. Standards on Plastics, 730–733, (October 1955),

(b) Pages 177 *and* 178 from June 1047 Photogrammatic Engineering, "The Physical Properties and Dimensional Stability of Safety Aerographic Film," J. M. Calhoun, which describes tests for measuring resistance to folding and tearing, and

(c) Leaflet P- 426 concerning the Elmendorf Tear Tester, Manufactured by the Thwing Albert Instrument Company, Philadelphia, Pa.

The Elmendorf apparatus tears the photographic material in such a way that the emulsion coating shows a ragged or feathered fracture line along the tear. The operator peels these feathered points back as far as possible and measures this distance in inches. The test was made at two relative humidities, 15 percent and 50 percent, the photographic material being permitted to reach equilibrium with the atmosphere at one or the other of these humidities before being used in the test.

EXAMPLE D

RF–M polyester base was pretreated with a 20 percent solution of dichloroacetic acid (DCA) in tetrahydrofuran, dried and washed in running distilled water at room temperature to remove excess acid, redried, and subbed by the 3 step process described above. The subbed base was overcoated with emulsion which was slow dried. Marked improvement in dry and excellent wet adhesion of emulsion was obtained as shown in the following table:

Base	Type Subbing	Dry Adhesion Before Processing, Peelback at—		Wet Adhesion After Processing	
		15% R.H.	50% R.H.	After 1 Day	After 6 Weeks
RF-M	3 step process	0.18″	0.8″	A	
RF-M	DCA pretreatment +3 step process	0.05	0.016	A-	A

NOTE.—2 mg. dm.^{2} of DCA was left on the base by the DCA treatment.

In the instance of polystystyrene supports, securing adhesion of the emulsion layer is usually not as great a problem as with certain other base materials. In a number of instances a thin cellulose nitrate sub on the polystyhene surface will provide adequate adherence at the interface between the polystyrne support and the emulsion layer of the present invention. However, there are a number of ways of treating the polystyrene base. The following will describe the application of copolymers of poly(ethyl acrylate coacrylic acid) to polystyrene film base to which has been bonded a thin layer (sub) of cellulose nitrate in such a way as to obtain superior adhesion at this interface. After drying, a surface consisting of the copolymer efficiently bonded to the cellulose nitrate layer forms the basis for adhesion of the emulsion layer.

The polymeric species proposed for application to film base which will be called "subbing polymers" consists of copoylmers of ethyl acrylate and acrylic acid formed in a solvent mixture which will attack the cellulose nitrate undercoat to the proper extent so that the surface becomes impregnated with a very thin layer of the copolymer which is presumably mechanically entangled with the cellulose nitrate. The copolymer is present in the free acid (uncharged form) when applied as the subbing polymer. When overcoated with a layer of the copolymer in its hydrophilic form (ammonium or sodium salt) together with a small amount of a cross-linking agent such as a bisepoxide or bisaziridine compound, the resulting coating will become insoluble and show excellent dry and wet adhesion.

The solution of subbing polymer is made up to about 15% solids in methanol. To this are added other solvents such as are described below to dilute the subbing polymer solution to the order of 1–2% polymer. The copolymers of ethyl acrylate and acrylic acid show excellent solubility in a wide range of solvents which are use to attack cellulose nitrate sub coats. These will be described below.

The subbings were designed principally with regard to the copoylmer of ethyl acrylate and acrylic acid which consists of three parts of the alkyl acrylate and 1 part of the acid. A series of coplymers ranging from 5 to 50 mole percent of the acid were used as the subbing polymers, and these were overcoated with solutions of the copolymer of ethyl acrylate and acrylic acid whose acid contents ranged from 15 mole percent to 50 mole percent. As will be shown, any subbing copolymer used could be coated with any copolymer in its hydrophilic form.

EXAMPLE E

A series of copolymers of ethyl acrylate and acrylic acid were made to give the following mole percentages of acrylic acid: 5, 15, 25, 35, and 50%. The polymers were dissolved in methanol to give solutions containing about 15% by weight of copolymer. These stock solutions were then added to a mixture of solvents to produce the following composition:

1%	polymer
15%	methyl cellosolve
15%	water
25%	acetone
44%	methyl acetone

The film base was first prime-coated with two thin cellulose nitrate sub layers of the following composition:

No. 1:

2.25%	cellulose nitrate
25.00%	ethylene dichloride
72.75%	methyl alcohol

No. 2:

2.25%	cellulose nitrate
97.75%	methyl alcohol

No. 2 is applied over No. 1 to provide a less contaminated cellulose nitrate surface.

This is then overcoated with a layer of polymer sub described above using the bead method of application. Aqueous coatings of an ammonium salt of the copolymer of ethyl acrylate and acrylic acid containing 25 mole percent of the acid were made on the above subbing and dried at 118° F. The aqueous solution contained 5% (on weight of polymer) of bis(2,3-epoxypropoxyethyl) ether as hardener. After aging for 7 days at 50% R.H., 75° F., all coatings gave excellent adhesion of the emulsion to the sub coating when placed in dilute alkali and in water.

EXAMPLE F

A copolymer of ethyl acrylate and acrylic acid was prepared to give 25 mole percent of acrylic acid. It was dissolved in methanol to give solutions containing about 15% by weight of the polymer. This stock solution was then added to a mixture of solvents to produce the following composition:

1%	copolymer
15%	methyl cellulose
15%	water
25%	acetone
44%	methyl alcohol

Dimensionally stable polystyrene base of the type referred to above was first coated with the following layers:

No. 1 resin U-coat:

4%	50/50 iso/normal buty methacrylate
25%	methyl alcohol
3%	butyl alcolhol
68%	hexane

No. 2 nitrate U-coat:

2%	cellulose nitrate (CWF type)
15%	methyl cellulose
83%	methyl alcohol

This was then overcoated with a layer of the polymer sub just described using the bead method of application.

Aqueous coatings of an ammonium salt of the copolymer of ethyl acrylate and acrylic acid which contained 25 mole percent of acrylic acid were made on the above subbing and dried at 118° F. The aqueous solution contained 4% (on weight of the copolymer of bis(2,3-epoxypropoxyetheyl)ether. After aging for 2 days at 50% R.H., 75° F., the adhesion of the emulsion to the sub coating was excellent in dilute alkali and water.

EXAMPLE G

A mixture of the following composition was coated on the polystyrene base described in Example F.

4.25 parts of the ammonium salt of the copolymer used in Example F
0.75 part gelatin
5.00 parts silver halide
90.00 parts water

Runs were made with the above mixture using 4% of bis(2,3-epoxypropoxyethyl)ether on the weight of the poly(ethyl acrylate coacrylic acid) and coatings were also made with 1% of triethylene melamine (on the weight of the copolymer). After aging for 2 days at 50% R.H., 75° F., the adhesion of both coatings was excellent in developer, fixer, and water wash.

In the examples just set forth the polymer solution was applied to a thin coat of cellulose nitrate. In certain instances other thin (prime) coats could be utilized. However, we prefer cellulose nitrate because of its wide range of solubility in various solvents.

It appears that the cross-linkage reaction occurring at the interface provides a set of primary chemical bonds which operate to fasten the overcoating to the base through the subbing layer which is well anchored to the base by mutual penetration of the polymers comprising the base and subbing.

The examples just set forth make use of ethyl acrylate and acrylic acid. Certain other monomers could be used. Some of these are: methyl and butyl acrylate, alkyl methacrylates and butadiene. Also, other unsaturated acids could be used as the comonomer. Among these would be: methacrylic acid, itaconic acid and crotonic acid. These will function somewhat similar to acrylic acid since they react with the cross-linking agents described.

After the support has been suitably prepared, as above discussed, to receive the emulsion layer, an emulsion layer in accordance with the present invention containing less than 0.45 gm. of gelatin per square ft. is then applied to the support. Such emulsion layer may be made up in various ways. Description of certain of these methods of preparing an emulsion layer will now be set forth.

Illustrative methods which may be used for making emulsions having less than 0.45 gram of gelatin per square foot are described in detail in Hewitson and McClintock U.S. Patent No. 2,618,556 patented November 18, 1952, and MacWilliam U.S. Patent No. 2,756,148 patented July 24, 1956. It appears sufficient to comment with respect to such methods to merely point out that one valuable feature in obtaining a low-gelatin, washed emulsion is the salt coagulation method of washing, since a large quantity of gelatin does not have to be used to solidify the emulsion by chilling, then noodling and washing in the conventional manner.

Also brief mention is made of the anionic soap emulsion washing type of process described in U.S. Patent 2,527,261 patented October 24, 1950.

Another method which may be used for making low-gelatin emulsions is described in detail in U.S. Patent 2,614,928 patented October 21, 1952.

Another and somewhat novel method is described below: A gelatino-silver halide emulsion of low-gelatin content may be prepared by adding a commercial enzyme to a normally sensitized gelatin emulsion. This produces essentially gelatin-free but optically sensitized silver halide grains which can then be redispersed in the desired amount of gelatin and coated as single layer or multilayer material or converted to packets or the like. In further detail, if a normally prepared silver halide emulsion with high gel concentration is first made and optically sensitized by known precedures and if the gelatin is then removed so that the silver halide grains retain their optical sensitivity, in many instances such procedure will be advantageous. It has been found that this can be accomplished by a suitable addition of a commercial enzyme (Rhozyme, for example) to normally sensitized high gelatin emulsions. Such treatment will yield essentially gelatin-free but optically sensitized silver halide grains. These grains can then be redispersed in an amount of gelatin so that coatings may be obtained in accordance with the above description, which coatings do not contain more than 0.45 gram of gelatin per square foot.

Various composite film products may be made up in accordance with the present invention wherein a relatively dimensionally stable polymeric base carries a low gelatin emulsion layer in accordance with the present invention. For a better understanding of such products reference may be made to the attached drawing forming a part of the present application.

In the attached drawing the figures represent sections of film product in accordance with the present invention, which sections are shown on a considerably exaggerated scale for clarity. It will further be kept in mind that the thickness of the various layers illustrated are not necessarily in proportion. Referring to FIG. 1, which represents the present invention in its simplest embodiment, 2 is the film base such as polymeric styrene or polyester flexible support. 3 represents the emulsion containing less than 0.45 gram per square foot of gelatin.

Referring now to FIG. 2, there is shown in this figure a film product more in accordance with the preferred embodiment of the present invention. In this figure, 4 represents the flexible support such as polystyrene or polyethylene terephthalate. This support contains one or more subs of the type extensively described above positioned between the support and the emulsion layer 6. In this preferred embodiment the emulsion layer would contain less than 0.35 gram of gelatin per square foot and preferably between 0.35 and 0.25 gram of gelatin per square foot. The preferred range of total gelatin, including the backing layer, is less than .90 gram of gelatin per square foot.

Film products as just described were made up by coating supports with gelatin-containing emulsions, certain of which emulsions were the low-gelatin type of the presen invention. These products were tested for overall dimensional stability. The results of these tests will be outlined in Table I below. It will be noted from these results in Table I that when the content of gelatin was kept below 0.45 gram per square foot and preferably below 0.35 gram per square foot, that the dimensional stability (percentage of dimensional change under varying humidity conditions) was substantially improved. For example, with respect to an 8 x 10 sheet of such photographic product, in accordance with the present invention there awas substantially no curl under certain humidity conditions.

Table I

A high contrast washed silver chlorobromide emulsion containing various amounts of gelatin was coated on a .005 inch polystyrene support. These washed emulsions containing low amounts of gelatin were prepared by the methods described above.

Support Backing, gm. of Gelatin per sq. ft.	Emulsion, gm. Gelatin per sq. ft.	Total Gelatin per sq. ft., gm.	Humidity Amplitude, Percent Dimensional Change From 10% to 70% R.H.	Curl at 20% R.H., 8x10 Sheet, in.
.63	.63	1.26	.10	+¾
.45	.45	.90	.075	----------
.34	.34	.68	.060	+3/16
.28	.28	.56	.050	----------

Similar improved results were obtained on other supports such as those made from polyesters.

It is believed that the film product of the present invention differentiates over the films now commercially available in that the product of the present invention contains less than 0.45 gram of gelatin per square foot on the emulsion side. Our preferred range lies below 0.35 gram of gelatin per square foot on the emulsion side. Polyester and polystyrene supports are preferred since these are the supports which give the best overall dimensional stability.

In the above description where we refer to various amounts of low gelatin such as 0.45 gram or 0.35 gram per square foot, these amounts may be measured in various ways. For example, the micro-Kjeldahl procedure used here for determination of gelatin in photographic emulsions is essentially that described by C. O. Willits and C. L. Ogg, in the Journal of the Association of Official Agricultural Chemists, 33, 179–188 (1950). This procedure is a determination of nitrogen which is calculated to gelatin content. It is necessary that the compositions examined do not contain significant amounts of other nitrogen-containing materials.

When we refer to percentage of dimensional change, such change may be measured in various ways. Certain satisfactory proceedings are set forth in Photogrammetric Engineering for June 1947, in the article "The Physical Properties and Dimensional Stability of Safety Aerographic Film," which describes on pages 182–185 shrinkage testing methods that could be used herein.

If the film support is thick enough, it will resist the tendency of the gelatin to deform it under changes in humidity, temperature, etc. In practice, it usually is desirable to coat on very thin film supports making the gelatin weight to support weight ratio an important factor. The following table gives *both* the amount of gelatin per square foot and the gelatin weight to support weight ratio. Polystyrene base has a specific gravity of 1.06 and the .0052" base used in these examples weighs 13.0 grams per square foot. From this table, it can be seen that the preferred range for the emulsion is less than .035 gram of gelatin per gram of support and preferably between .025 gram and .020 gram of gelatin per gram of support. For total gelatin, the preferred range is less than .070 gram of gelatin per gram of support and preferably between .050 gram and .040 gram of gelatin.

Support Backing Layer		Emulsion Layer		Total Gelatin		Percent Dimensional Change from 10%–70% R.H.
Gelatin, gm./sq. ft.	Gelatin, gm./gm., Support	Gelatin, gm./sq. ft.	Gelatin, gm./gm., Support	Gelatin, gm./sq. ft.	Gelatin, gm./gm., Support	
.63	.0485	.63	.0485	1.26	.097	.10
.45	.0346	.45	.0346	.90	.069	.075
.34	.0262	.34	.0262	6.8	.052	.060
.28	.0216	.28	.0216	.56	.043	.050

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. A photographic film product having good dimensional stability comprised of

(A) a film base having a thickness of from about .004 to .008 inch selected from the group consisting of polystyrene film base and polyethylene terephthalate film base,

(B) at least one non-gelatin-containing sub layer on said film base, and

(C) a light-sensitive silver halide emulsion layer comprised of gelatin as the sole binder material, the gelatin content of said layer being from about 0.2 to 0.45 gram per square foot of film base,

the total gelatin content of the photographic film product being less than about 0.90 gram per square foot of film base.

2. A photographic film product having a good dimensional stability comprised of

(A) a polystyrene film base having a thickness of from about .004 to .008 inch,

(B) at least one non-gelatin-containing sub layer comprised of cellulose nitrate on said film base, and

(C) a light-sensitive silver halide emulsion layer comprised of gelatin as the sole binder material, the gelatin content of said layer being from about 0.25 to 0.35 gram per square foot of film base,

the total gelatin content of the photographic film product being less than about 0.90 gram of gelatin per square foot of film base.

3. A photographic film product having good dimensional stability comprised of

(A) a polyethylene terephthalate film base having a thickness of from about .004 to .008 inch.

(B) at least one non-gelatin-containing sub layer comprised of an acrylate polymer, and

(C) a light-sensitive silver halide emulsion layer comprised of gelatin as the sole binder material, the gelatin content of said layer being from about 0.25 to 0.35 gram per square foot of film base,

the total gelatin content of the photographic film product being less than about 0.90 gram of gelatin per square foot of film base.

4. A photographic film product having good dimensional stability comprised of

(A) a polystyrene film base having a thickness of from about .004 to .008 inch,

(B) a sub layer comprised of cellulose nitrate disposed on the film base,

(C) a sub layer comprised of a copolymer of ethyl acrylate and acrylic acid on sub layer (B), and

(D) a light-sensitive silver halide emulsion layer comprised of gelatin on the sub layer (C), the gelatin content of said emulsion layer being from about 0.25 to 0.35 gram per square foot of film base,

the total gelatin content of the photographic film product being less than about 0.90 gram of gelatin per square foot of film base.

5. A photographic film product having good dimensional stability comprised of

(A) a polyethylene terephthalate film base having a thickness of fromabout .004 to .008 inch,

(B) a sub layer comprised of a terpolymer of acrylic acid, n-hexylacrylate, and vinylchloride on the film base

(C) a sub layer comprised of cellulose nitrate on layer (B),

(D) a sub layer comprised of gelatin on layer (C), and

(E) a light-sensitive silver halide emulsion layer comprised of gelatin as the sole binder material on the sub layer (D), the gelatin content of said emulsion layer being from about 0.25 to 0.35 gram per square foot of film base,

the total gelatin content of the photographic film product being less than about 0.90 gram of gelatin per square foot of film base.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

atent No. 3,201,250

August 17, 1965

George M. Coryell et al.

It is hereby certified that error appears in the above numbered pat- nt requiring correction and that the said Letters Patent should read as orrected below.

Column 5, line 34, for "Photogrammatic" read -- Photo- rammetric --; column 6, line 1, for "polystystyrene" read -- olystyrene --; line 5, for "polystyhene" read -- polystyrene -; line 6, for "polystyrne" read -- polystyrene --; line 19, or "copoylmers" read -- copolymers --; line 41, for "copoylmer" ead -- copolymer --; same column 6, line 43, for "coplymers" ead -- copolymers --; column 9, line 27, for "awas" read -- s --; columns 9 and 10, Table I, fifth column, line 3 thereof, or "6.8" read -- .68 --; column 11, line 43, for "fromabout" ead -- from about --.

Signed and sealed this 29th day of March 1966.

EAL)
test:

NEST W. SWIDER
testing Officer

EDWARD J. BRENNER
Commissioner of Patents