Jan. 27, 1942. G. F. NADEAU ET AL 2,271,228

PHOTOGRAPHIC FILM SUBBED WITH HARDENED GELATIN

Filed Sept. 16, 1939

FIG. 1.

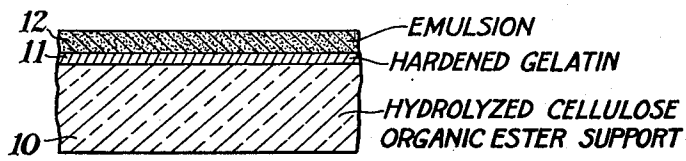


FIG. 2.

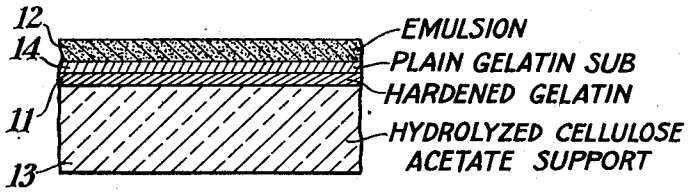


FIG. 3.

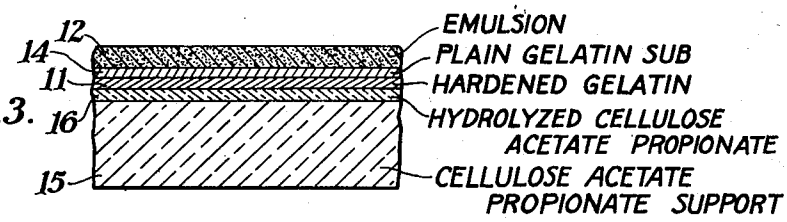


FIG. 4.

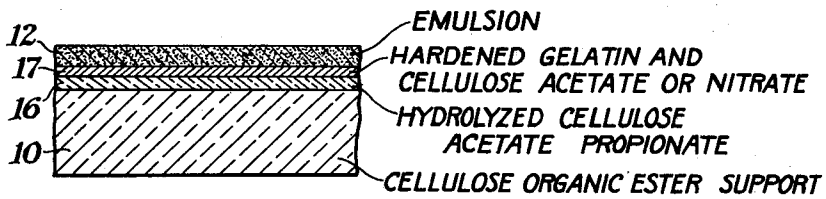


FIG. 5.

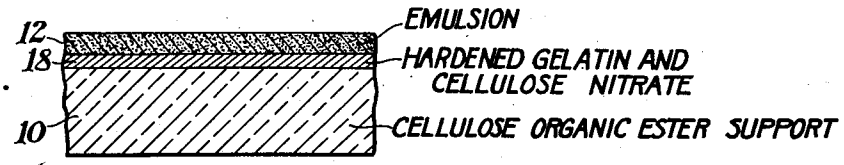
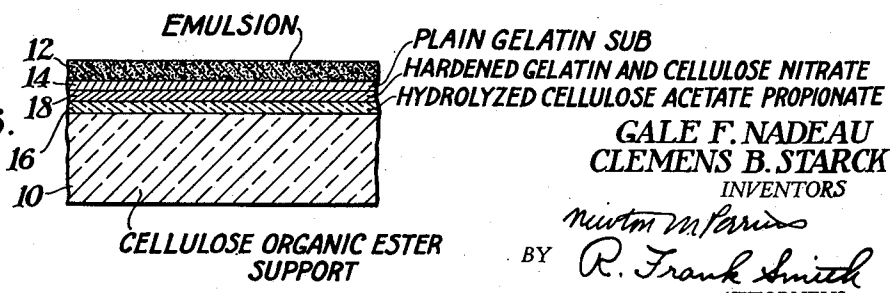


FIG. 6.



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PHOTOGRAPHIC FILM SUBBED WITH HARDENED GELATIN

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14 Claims. (Cl. 95—9)

This invention relates to photographic film and particularly to a method of subbing involving the use of hardened gelatin.

It is known that a gelatino silver halide emulsion cannot be applied directly to a cellulose organic derivative film support. Intermediate or subbed layers must be applied between the support and the emulsion and each of these layers must adhere to the layer adjoining it. The degree of adhesion of the layers must be properly controlled in order to avoid the formation of a product which is brittle or in which the layers peel from the support. If the degree of adhesion is too great, the film is brittle and the layers crack when the film is bent. If the adhesion is too slight, the layers are likely to peel or strip from the support when the film is dry or when it is treated in the developing or fixing baths or other processing solutions.

Although many attempts have been made to use a subbing technique involving the direct application of gelatin solutions to cellulose organic derivative supports, none of these procedures has been generally acceptable, due to the inability of the process to give good stripping and brittleness qualities without sacrificing one for the other. The ease with which cellulose organic ester can be subbed with gelatin increases as the degree of hydrolysis of the cellulose ester is increased, it being practically impossible to sub a fully esterified organic ester with gelatin. It has been found that as the degree of hydrolysis is increased, dry stripping properties increase rapidly at first, then increase to a less degree. As the hydrolysis increases, however, more trouble is experienced with wet stripping or frilling of the film during processing, and it has heretofore been impossible to overcome this objection.

From a subbing standpoint, attempts have been made to harden the gelatin sub chemically in order to reduce its moisture susceptibility. As is known, this is common practice in the preparation of photographic emulsions. Unfortunately, three difficulties have been encountered which heretofore have made this variation in subbing procedure impractical. In the first place, most hardening agents are not compatible with the gelatin sub. Ordinary hardening agents not only show very poor solubility in the subbing formula used but many of them cause an electrolytic precipitation of the gelatin. In the second place, the use of such hardening agents as are soluble or otherwise compatible with the sub has resulted in poor stripping of the finished film if the base is allowed to age for some weeks before being emulsion coated. For example, the use of formaldehyde in a gelatin sub produces a film showing good wet stripping if the film base is coated with emulsion within about two weeks after its preparation. This is impractical, however, because it is frequently necessary to keep stocks of base on hand and formaldehyde, therefore, cannot be used in gelatin subs as a hardening agent. A third difficulty encountered in attempting to harden gelatin subs arises from the fact that these subs are always strongly acidic in nature and many of the hardening agents used operate best in neutral or alkaline solutions. It follows, therefore, that most of the hardeners that have been approved for photographic uses are inoperable in gelatin subs. Apparently the hardening action of many materials is strongly inhibited by the presence of either acid or organic solvent. As a result, many materials which harden well in aqueous mixtures cannot be used for subbing properties.

We have found that inorganic salts of trivalent chromium, such as chromic chloride, function satisfactorily as hardening agents for gelatin subbing solutions. These compounds possess none of the disadvantages referred to and, at the same time, function as hardeners for subs so that wet stripping or frilling of photographic film can be controlled without otherwise strengthening the sub to the point of producing brittleness of the film. Chromic chloride, for example, is quite soluble in the usual subbing formulas, hardens the gelatin as desired, and the subbed support can be kept for a considerable length of time without after-hardening to the point that the film has poor stripping qualities. Furthermore, chromic chloride does not decrease the stability of the gelatin sub due to electrolytic precipitation of the gelatin.

In addition to chromic chloride, other inorganic salts of trivalent chromium which may be used are chrome alum and chromic nitrate. In some cases, however, chrom alum tends to produce precipitation of the gelatin. Chromic nitrate, although it must be used in slightly greater quantities to produce satisfactory hardening, is satisfactory in this respect. The hardening agent which we prefer to use, therefore, is chromic chloride.

In the accompanying drawings, Figs. 1 to 6 are sectional views of photographic film subbed according to our invention.

This invention comprises, in its broader aspects, the use of a gelatin sub hardened with an inorganic salt of trivalent chromium such as

chromic chloride. These compounds are unique in respect to their favorable action in gelatin subbing solutions and are satisfactory for this purpose whereas many of the usual hardening agents are not. Among the hardening agents that have been tried without success may be mentioned aluminum chloride, thorium nitrate, zirconium oxychloride, lanthanum chloride and several organic hardening agents such as acetonyl acetone, formaldehyde and diacetyl.

The adhesion of the sub to the base or undercoat may be improved by adding cellulose nitrate or a cellulose organic ester to the hardened gelatin and the stripping and brittleness qualities of the film controlled in this way. For example, incorporation of a relatively small quantity of cellulose nitrate in the hardened gelatin sub greatly improves adhesion of the emulsion to the base and particularly improves stripping qualities when the film is heated for the purpose of drying after development, fixation, and washing.

In operating the invention, a gelatin sub is selected which will give the desired series of dry stripping and brittleness results but which would in many instances show poor wet stripping, and chromic chloride is added to it until the desired wet stripping results are obtained. Brittleness of the film is also controlled by the addition of cellulose nitrate or cellulose organic esters to the hardened gelatin and it is frequently desirable to control brittleness in this way rather than by the composition of the gelatin alone.

The amount of chromic chloride hardener in the gelatin solution may vary from about ½% to about 2½% of the weight of gelatin contained in the sub. It has been found that somewhat lower concentrations of chromic chloride are effective and that higher concentrations may be used after the hardening becomes so severe that poor stripping results. We have found that taking all factors into consideration, a quantity of chromic chloride from 1 to 1½% of the weight of the gelatin appears to be an optimum concentration.

In the accompanying drawing, we have shown various enlarged sectional views of photographic film subbed according to modifications of our invention. As shown in Fig. 1, the support **10** of an organic acid ester of cellulose which has been hydrolyzed, is coated with a layer **11** of gelatin hardened according to our invention. On the hardened gelatin layer **11** is coated the sensitive emulsion layer **12**. This represents a departure from the usual subbing procedure since it is possible by the use of our gelatin hardeners to obtain a gelatin subbing solution which may be coated directly on a hydrolyzed cellulose organic ester support. It has hitherto been possible to coat gelatin directly on cellulose nitrate supports but it has been practically impossible to coat gelatin onto cellulose organic ester supports to form a product acceptable to high commercial standards.

Fig. 2 shows a similar film in which the support **13** is represented as being composed of hydrolyzed cellulose acetate. On the support **13** is coated a hardened gelatin layer **11** and a plain gelatin subbing layer **14** is coated over the subbing layer **11**. This gelatin layer **14** is frequently of value in securing adhesion of the emulsion layer **12**.

As shown in Fig. 3, a support **15** of cellulose acetate propionate which may be hydrolyzed or fully esterified is coated with a layer **16** of hydrolyzed cellulose acetate propionate which is compatible with the ester of the base **15**. We may also use successive layers of more hydrolyzed cellulose ester, such as a layer of cellulose acetate propionate hydrolyzed to a precipitation value of 95%, followed by a cellulose acetate propionate hydrolyzed to a precipitation value of 80%. On the hydrolyzed cellulose acetate propionate layer **16**, there are coated successively the hardened gelatin layer **11** and the plain gelatin subbing layer **14**, followed by emulsion layer **12**. A subbing technique of this nature is advantageous where a substantially fully esterified cellulose organic ester support is used. The layer coated on it can be hydrolyzed as far as possible without destroying its compatibility with the ester of the base and the hardened gelatin sub coated on it. The wet stripping properties of the film are controlled by the amount of hardening agent added to the gelatin and emulsion stripping is controlled by the very thin gelatin layer coated over the hardened gelatin sub.

In Fig. 4, we have shown a modification in which the support **10** of cellulose ester is coated with a hydrolyzed organic acid ester such as hydrolyzed cellulose acetate propionate **16**. Over this hydrolyzed cellulose ester layer **16** there is coated a layer **17** of hardened gelatin and cellulose nitrate or cellulose acetate. Over the layer **17** there is coated the emulsion layer **12**. As described above, a technique of this type is frequently desirable in controlling stripping and brittleness properties of the film.

Fig. 5 shows a modification in which the support **10** of cellulose organic ester is coated directly with a mixture of hardened gelatin and cellulose nitrate **18**. This is followed directly by the emulsion layer **12**. This modification is similar to that shown in Fig. 1 except that cellulose nitrate is mixed with the hardened gelatin sub. As pointed out above this addition of cellulose nitrate improves the adhesion of the emulsion to the base when the film is dried after photographic processing, that is after development, fixing and washing.

In Fig. 6, the cellulose organic ester support **10** is coated with a layer of hydrolyzed cellulose acetate propionate **16** followed by a layer **18** of hardened gelatin and cellulose nitrate. This is followed by a plain gelatin layer **14** and the emulsion layer **12**. In this case as in the case of the modification shown in Fig. 3, the hydrolyzed cellulose acetate propionate sub **16** or other hydrolyzed cellulose mixed organic ester may be substituted by layers of successively hydrolyzed cellulose mixed organic esters.

Our invention will be further described by reference to the following examples, which are illustrative only.

Example 1

A photographic film support of cellulose acetate hydrolyzed to a precipitation value of 90 and an acetyl content of 40.5% is coated with a subbing solution of the following composition.

Gelatin	per cent	0.9
Glacial acetic acid	do	1.0
Water	do	13
Acetone	do	70
Methyl Cellosolve	do	5
Methyl alcohol	do	10.1
Chromic chloride	per cent of the weight of gelatin	2½

After drying, this subbing layer is coated with the usual emulsion layer. The amount of acetic acid in this formula may vary from 0.6% to 1.5% and the amount of water from 6% to 13%.

Example 2

A film base of cellulose acetate propionate hydrolyzed to a precipitation value of about 97% acetyl 30.0%, propionyl 16.0% coated with a hydrolyzed cellulose acetate propionate having a precipitation value of about 88%. This cellulose ester is more hydrolyzed than the ester of the support but is compatible with it. The coating composition used for the undercoat is as follows:

	Per cent
Hydrolyzed cellulose acetate propionate (88% precipitation value)	3
Acetone	60
Methyl Cellosolve	10
Methyl alcohol	27

This is followed by a hardened gelatin sub of the following composition:

Gelatin	per cent	1
Acetic acid	do	1
Acetone	do	60
Water	do	4 to 12
Methyl alcohol	do	27 to 35
Chromic chloride per cent of the weight of gelatin		1 to 2

On the hardened gelatin layer there is coated the usual silver halide emulsion layer.

Example 3

A photographic film base of cellulose acetate propionate having a precipitation value of about 98% is coated with a solution of cellulose acetate propionate hydrolyzed to a precipitation value of about 95%. The composition of this solution is as follows:

	Per cent
Hydrolyzed cellulose acetate propionate (precipitation value 95%)	3
Acetone	60
Methyl Cellosolve	10
Methyl alcohol	27

This layer is followed by a mixed gelatin and cellulose acetate sub of the following composition

Gelatin	per cent	1
Cellulose acetate (90% precipitation value, 40.5% acetyl)	do	0.8
Acetic acid	do	1.0
Acetone	do	60
Methyl Cellosolve	do	10
Methyl alcohol	do	16.2 to 24.2
Chromic chloride per cent of the weight of gelatin		1½

On this hardened gelatin layer there was coated a plain gelatin layer of the following composition:

	Per cent
Gelatin	3
Water	40
Methyl alcohol	56.7
Acetic acid	0.3

A gelatino-silver halide emulsion layer was coated on the plain gelatin layer.

Example 4

A photographic film support of cellulose acetate (cellulose triacetate) having a precipitation value of about 98% was coated with a layer of hydrolyzed cellulose acetate having a precipitation value of about 92%. This coating solution had the following composition:

	Per cent
Hydrolyzed cellulose acetate (95% precipitation value)	1 to 3
Ethylene dichloride	40 to 80
Methyl alcohol	17 to 59

This cellulose acetate undercoat was coated with a subbing solution of hardened gelatin and cellulose nitrate having the following composition:

	Per cent
Gelatin	1.5
Cellulose nitrate	0.3
Acetone	60
Methyl Cellosolve	10
Water	6
Methyl alcohol	2.2

To this solution is added chromic chloride 2% of weight of gelatin. The sensitive emulsion layer may be coated directly on this subbing layer of hardened gelatin and cellulose nitrate.

Example 5

A photographic film base of fully esterified cellulose acetate propionate is coated with a cellulose acetate propionate solution in which the cellulose ester consists of a mixture of 60% cellulose acetate propionate hydrolyzed to a precipitation value of 95% and 40% cellulose acetate propionate hydrolyzed to a precipitation value of 88%. This mixture adheres well to the fully esterified type of base. The coating solution used may have the following composition:

	Per cent
Cellulose ester	1 to 3
Ethylene dichloride	40 to 80
Methyl alcohol	17 to 59

This overcoat is coated with a subbing solution of hardened gelatin and cellulose nitrate having the following composition:

	Per cent
Gelatin	1.5
Cellulose nitrate	0.6
Acetone	70
Methyl Cellosolve	10
Water	6
Methyl alcohol	11.9

To this solution is added acetic acid equal to the weight of gelatin, and chromic chloride equal to 1% of the weight of gelatin. Over the hardened gelatin and cellulose nitrate layer there is coated a gelatin subbing layer of the following composition:

	Per cent
Gelatin	1 to 3
Water	10 to 40
Methyl alcohol	57 to 89

This gelatin subbing solution may also contain a dispersing agent, an anti-static compound and a gelatin hardener. The plain gelatin subbing layer applied at this state accomplishes two purposes: it improves adherence of emulsion layer to the film base since the increased concentration of the cellulose nitrate in the mixed sub tends to reduce adherence of the emulsion layer to the base. In the case of X-ray base it also functions as an antistatic layer.

The usual gelatino-silver halide emulsion layer is then coated directly on the gelatin subbing layer.

In Examples 4 and 5 in which cellulose nitrate is mixed with the hardened gelatin sub, the cellulose nitrate preferably used is one which has an alcohol solubility of 30% to 100% and nitrogen content of 11% to 12%. The proportion of cellulose nitrate in the mixed sub may be varied in the case of Example 4 from about 0.1% to about 0.3% and in the case of Example 5 from about 0.3% to 1.5%.

The solvent included in the subbing solutions may also be varied. The amount of acetone may range from 20% to 80% and the amount of water from 6% to 10% or higher. The amount of methyl alcohol may be reduced or omitted entirely.

We have referred in the above specification to the precipitation value of a number of cellulose esters. Precipitation value is the customary test used to determine the degree to which a cellulose organic ester has been hydrolyzed. As the degree of hydrolysis increases, the precipitation value decreases. The test for precipitation value is carried out as follows:

Five grams of the dry cellulose ester are accurately weighed and placed in a wide mouth 12 oz. bottle. To this are added 100 cc. of acetone (commercial grade of 99% or better), the mixture is stirred until homogeneous. (The bottle should be closed during the stirring with a rubber stopper fitted with a shaft for the stirrer.) To this dope is added slowly from a pipette and with thorough stirring, 150 cc. of a mixture consisting of 2 parts of distilled water and 1 part acetone by volume. Care should be taken to keep the solvents and mixtures at 20° C. wherever volumes are being measured.

At the end of the addition of the acetone-water mixture, a mixture is obtained containing 40% water by volume (neglecting contraction) in which is suspended the precipitated ester. This is allowed to stand for 12 hours at 20° C. At the end of this time precipitation has reached equilibrium and proceeds no further, and during the same time settling of the precipitate occurs. 25 cc. of the clearest portion (supernatant solution) are removed with a pipette. This 25 cc. is centrifuged in stoppered bottles at high speed until the liquid is perfectly clear. Exactly 5 cc. of the clear liquids are removed with a pipette and evaporated to dryness on a tarred watch glass. If W is the weight of the residue in grams, the precipitation value which equals the per cent ester precipitated,

$$=100-\left(Wx\frac{250}{5}\times\frac{1}{5}\times 100\right)$$

$$=100-1000W$$

We have also referred in our specification to stripping and brittleness or flexibility tests. The customary methods of determining whether a film has satisfactory stripping and brittleness properties are as follows:

The dry stripping test is carried out as follows: A piece of the complete emulsion-coated film of a convenient size, say, 6 inches wide by 40 inches long, is held at one end with both hands with the emulsion side toward the operator and is then torn lengthwise with successive quick motions of one hand, the tearing generally being carried out at a slight angle to the edge of the strip in order to obtain an oblique tear. The tears thus produced are more or less jagged. An attempt is now made to pull back the emulsion coating from the film with the fingernails and the degree to which the emulsion separates from the support is a measure of its adherence. It will, of course, be understood that the standards of emulsion adherence will vary for different types of film and what is considered satisfactory for one film may not be satisfactory for another. For example, stripping (emulsion adherence) is said to be satisfactory for X-ray film if the emulsion cannot be stripped back more than three or four inches.

The wet stripping test is carried out as follows: A strip of the emulsion-coated film of convenient size is soaked in water at 70° F. for ten minutes, or is passed through the regular photographic developing, fixing, and washing solutions for the usual time It is then removed from the water and fixed on a flat surface with the emulsion side up. The emulsion is then gouged or creased with the fingernails at points near the middle and end of the strip, each nail scratch tearing the emulsion away from the support to a certain extent. The scratched places are then rubbed with considerable force with the balls of the fingertips for several seconds. A film is said to have satisfactory wet stripping (emulsion adherence) properties when no peeling, or substantially no peeling, of the emulsion occurs as a result of this rubbing action. Wet stripping is said to be unsatisfactory when an appreciable or large amount of the emulsion comes off. For most types of film it should not be possible to remove pieces wider than ¼ inch by this test.

The test customarily employed for determining the brittleness of X-ray and portrait film is carried out as follows: A strip of film of convenient size is heated for two hours in a brittleness oven in which air having a controlled relative humidity of 10–20% and a temperature of 80–100° F. is circulated. The film is then removed from the oven and folded at ten different places along the strip by pressing the fold suddenly between the forefinger and the thumb. If the film is brittle, this sudden folding will cause it to break or snap in two at the fold. The flexibility may be defined in terms of freedom from brittleness which may be figured directly in percentages from the results of the test. For example, a film is said to be 60% free from brittleness if it ruptures at only four out of ten folds.

Another test for brittleness customarily applied to motion picture film consists in heating a sample of the film at 90–100° C. for 10 minutes, after which the film is folded between the thumb and finger in several places, with the emulsion side up. If a break occurs all the way across, the film is said to be "brittle." If the break extends only half way across, the film is said to be "slightly brittle" while if the break does not extend more than a quarter of the way across, the film is said to be "very slightly brittle." If no break occurs, the film is "non-brittle."

Numerous important advantages are achieved by the use of chromic chloride or other chromium salts as hardeners for gelatin subbing solutions according to our invention. One advantage is the control of stripping or frilling without otherwise strengthening the sub to the point of producing brittleness in the film. Another advantage is the keeping made possible without after-hardening of the subbing solution before the film is coated with emulsion. A further advantage in this type of sub is in the relatively high water content which can be tolerated. The stability of the sub is greatly improved by the increased

water and, due to the hardening of the sub, bad stripping does not result. A further advantage of this type of subbing is in the electrification behavior of the film base. In order to eliminate static in coating X-ray film, for example, it is necessary to apply an anti-static gelatin coating to both sides of the film base before emulsion coating it. By the use of a single gelatin sub hardened according to our invention, good electrification properties of the base result and it is possible to save the expense of two applications on the support and at the same time simplify the production of photographic film.

The examples and modifications described in the present specification are illustrative only and it is to be understood that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. A photographic film free from stripping and brittleness, comprising a cellulose ester support and an emulsion layer, and between said support and said emulsion layer, a layer comprising gelatin hardened with chromic chloride.

2. A photographic film free from stripping and brittleness, comprising a cellulose organic ester support, and in order thereon, a layer comprising gelatin hardened with chromic chloride, a plain gelatin layer and an emulsion layer.

3. A photographic film free from stripping and brittleness, comprising a cellulose organic ester support, and in order thereon, a layer of hydrolyzed cellulose organic ester, a layer comprising gelatin hardened with chromic chloride, and an emulsion layer.

4. A photographic film free from stripping and brittleness, comprising a cellulose organic ester support, and in order thereon, a layer of hydrolyzed cellulose organic ester, a layer of cellulose ester mixed with gelatin hardened with chromic chloride, and an emulsion layer.

5. A photographic film free from stripping and brittleness, comprising a cellulose organic ester support, and in order thereon, a layer of hydrolyzed cellulose organic ester, a layer of hydrolyzed cellulose organic ester mixed with gelatin hardened with chromic chloride, and an emulsion layer.

6. A photographic film free from stripping and brittleness, comprising a cellulose organic ester support, and in order thereon, a layer of hydrolyzed cellulose organic ester, a layer of cellulose nitrate mixed with gelatin hardened with chromic chloride, and an emulsion layer.

7. A photographic film free from stripping and brittleness, comprising a cellulose acetate support, and in order thereon, a layer of hydrolyzed cellulose acetate, a layer of cellulose ester mixed with gelatin hardened with chromic chloride, a plain gelatin layer, and an emulsion layer.

8. A photographic film free from stripping and brittleness, comprising a cellulose acetate support, and in order thereon, a layer of hydrolyzed cellulose acetate, a layer of hydrolyzed cellulose acetate mixed with gelatin hardened with chromic chloride, a plain gelatin layer, and an emulsion layer.

9. A photographic film free from stripping and brittleness, comprising a cellulose organic ester support, and in order thereon, a layer of cellulose nitrate, a layer comprising gelatin hardened with chromic chloride, and an emulsion layer.

10. A photographic film free from stripping and brittleness, comprising a cellulose organic ester support, and in order thereon, a layer of hydrolyzed cellulose mixed organic ester, a layer of a more hydrolyzed cellulose organic mixed ester, a layer of cellulose nitrate and gelatin hardened with chromic chloride, and an emulsion layer.

11. A photographic film free from stripping and brittleness, comprising a cellulose organic ester support, a layer of cellulose acetate propionate hydrolyzed to 95% precipitation value, a layer of cellulose acetate propionate hydrolyzed to 80% precipitation value, a layer of cellulose nitrate and gelatin hardened with chromic chloride, and an emulsion layer.

12. A photographic film free from stripping and brittleness, comprising a cellulose organic ester support, a layer of cellulose acetate propionate hydrolyzed to 95% precipitation value, a layer of cellulose acetate propionate hydrolyzed to 80% precipitation value, a layer of cellulose nitrate and gelatin hardened with chromic chloride, a plain gelatin layer, and an emulsion layer.

13. A photographic film free from stripping and brittleness comprising a cellulose organic ester support, an emulsion layer and between said support and said emulsion layer, a layer of cellulose nitrate mixed with gelatin hardened with a halide of trivalent chromium.

14. A photographic film free from stripping and brittleness comprising a cellulose organic ester support, and, in order thereon, a layer of cellulose nitrate mixed with gelatin hardened with an inorganic salt of trivalent chromium selected from the group consisting of chromic nitrate and chromic chloride, and an emulsion layer.

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