

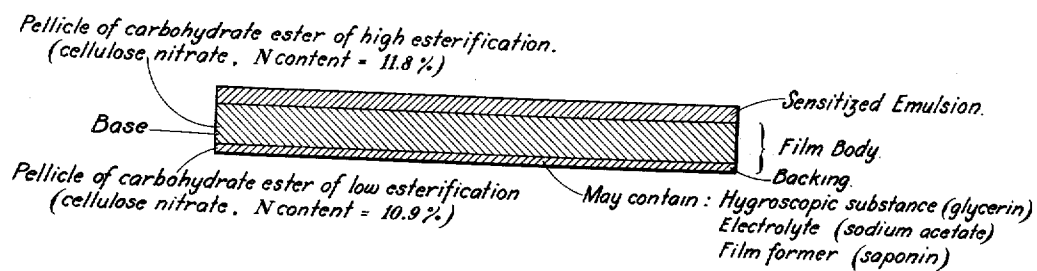
Jan. 19, 1926.

E. C. PITMAN

1,570,076

NONSTATIC PHOTOGRAPHIC FILM

Filed Sept. 16, 1920



E. C. Pitman, Inventor

By his attorney J. R. Squair.

UNITED STATES PATENT OFFICE.

EARLE C. PITMAN, OF PARLIN, NEW JERSEY, ASSIGNOR TO E. I. DU PONT DE NEMOURS & COMPANY, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE.

NONSTATIC PHOTOGRAPHIC FILM.

Application filed September 16, 1920. Serial No. 410,746.

To all whom it may concern:

Be it known that I, EARLE C. PITMAN, a citizen of the United States, and a resident of Parlin, in the county of Middlesex and State of New Jersey, have invented a certain new and useful Nonstatic Photographic Film, of which the following is a specification.

This invention relates to photographic films having provisions for the elimination of discharges of static electricity. With the ordinary film these discharges occur when the film is stripped from the casting surface, when it is run rapidly through a cinematographic camera and under various other circumstances. Such discharges cause markings on the sensitized emulsion by premature exposure thereof. It is an object of the invention to provide a film which, for practical purposes of manufacture and use, will be free from static electricity, and it is also an object to improve generally upon films of the character indicated.

For convenience and brevity of description I use the term "film" to denote the entire article, whether or not the article includes a sensitized emulsion; the term "film body" to denote the entire emulsion support whether or not that support is composed of a plurality of layers, sub-films or pellicles; the term "backing" to denote a layer of a composite film body, which lies adjacent the other side of the film body from the side intended to directly carry the emulsion; and I use the term "base" to denote the portion of a composite film body which is intended to carry the backing at one side and the emulsion at the other and to form or include the principle strength-giving portion of the film. On occasion, as will appear from the context, I use the term "base" (or pellicle base) to also indicate the substance, as cellulose nitrate, which is the primary substance used to form a pellicle.

In the accompanying drawing I have, without restricting my invention thereto, shown a film embodying my invention, the

view being a conventional, exaggerated, cross-sectional showing.

According to my invention, I use in the film body a substance, or substances, which will make the body, either as a whole, or at its backing where one is used, more electrically conductive than is the ordinary film. In this way, I provide that such static charges as tend to be generated shall leak away, be neutralized, or be evenly distributed, before they can accumulate in such a way, or to such amount, as to be liable to harmful discharge.

Thus, I may incorporate in the body a hygroscopic substance such as glycerine; an electrolyte such as sodium or ammonium acetate, or magnesium nitrate; or a "film former" such as saponin, alkali salts of unsaturated fatty acids (such as sodium sulphoricinoleate), alkali salts of egg albumin, or alkali salts of aromatic sulphonic acids; or I may use any of the various combinations of substances of these general characters that I may desire, the substances selected for any specified case to be soluble in the particular solvent mixture used for making the pellicle in which the substances are to be incorporated, and to be such as not to cause precipitation of the pellicle base, as nitrocellulose, used for the pellicle. The hygroscopic substance increases the conductivity by increasing the moisture content, and the electrolyte increases the conductivity of any moisture present. A "film former," acts to convert the isolated drops of moisture, collecting on the film, into a homogeneous continuous film, thereby increasing conductivity. Both the electrolyte and the film former are, of course, valuable whether or not a hygroscopic substance is used also, as some moisture is present in any case.

In general, and as previously indicated, a film body, i. e. the entire emulsion support, may consist of one layer only; or may consist of a plurality of layers, one of the layers being the backing and the remainder of the body being the base or principal strength

giving layer or layers of the film body.

When incorporating the various substances, e. g. sodium acetate and so on, in accordance with the invention, they may be placed in a film body not comprising a backing and made from any desired pellicle base, e. g. cellulose nitrate; or such substances may be, in the first instance, placed in a backing and such backing applied to any desired base layer. The backing may be one which primarily functions merely by virtue of the substances and, so, may not contain a pellicle base, e. g. nitrocellulose; or it may contain a pellicle base of any suitable character and either having substantially the same conductivity as the pellicle base used in making the base of the film, or having a conductivity somewhat greater than that of the pellicle base used in making the base of the film and enabling the pellicle base of the backing to itself serve in giving the backing a superior conductivity.

As to the use for the backing of a pellicle base which is itself of superior conductivity, I may apply a backing layer of carbohydrate ester of relatively low esterification, e. g. cellulose nitrate of 11½% or less nitrogen content, that is, of not over 11½% nitrogen content. I have found that cellulose nitrate decreases in hygroscopicity and in conductivity as the nitrogen content increases, though it increases in strength, so that cellulose nitrate of not over 11½% nitrogen content is more hygroscopic and more conductive than cellulose nitrate of more than 11½% nitrogen content; yet experience has shown that, if proper strength is to be secured in a cellulose nitrate film, then a film primarily of cellulose nitrate of more than 11½% nitrogen content is a practical necessity, despite the fact that, used alone, it is liable to static discharges due to its non-conductivity. So, in carrying out my invention, I apply a backing of cellulose nitrate of 11½% or less nitrogen content, preferably about 10.9%, to a base of cellulose nitrate having more than 11½% nitrogen content, preferably about 11.8% to 12%. In this way I produce a nitrocellulose film which has the strength demanded by the trade and yet is conductive and substantially non-static. As will be understood, a film of the character just indicated may, if desired, contain no added hygroscopic, electrolytic or film-forming substances and yet present the advantage of conductivity to a marked degree. In such cases, any suitable formulas for the base and the backing solutions may be used; conveniently, the below-given formulas "4," and "1" or "4," each with the sodium acetate omitted, may be used for the base, and the backing, respectively.

While the above mentioned nitrocellulose backing is highly advantageous of itself

either when applied to any suitable film base or, particularly, when applied to the mentioned nitrocellulose film base, I have found, as previously indicated, that the incorporation in such a backing of conductivity-increasing substances, such as a hygroscopic substance, an electrolytic substance, or a film-forming substance, or any combinations of these, gives a particularly satisfactory film.

The mechanical operations of making films in accordance with my invention will be evident to those skilled in the art, the casting of films, and similar operations, as such, being of course well known in the art. The backing solution may be applied, and the solvents evaporated to give the backing, in any convenient manner. Below I give formulas illustrative of films embodying my invention, it being understood that I do not restrict the invention to the examples given. In the formulas, figures refer to parts by weight.

(1) For a backing containing an electrolyte, sodium acetate, the following formula may be used:—

	Approximate range.	Preferred.
Cellulose nitrate (dry).....	4 to 16	8
Sodium acetate (NaAc 3H ₂ O).....	0.25 to 16	1
Wood alcohol.....	100 to 150	120
Acetone.....	10 to 50	20
Fusel oil.....	10 to 50	40
Amyl acetate.....	10 to 40	20

In making up, to the combined solvents add (a) the sodium acetate and (b) the cellulose nitrate, in order.

(2) For a backing containing an electrolyte, sodium acetate, and a film former, saponin, the formula, as to ingredients, ranges and preferred amounts, may be the same as for "1" except that it should in addition include approximately 0.005 to 0.20 part, preferably 0.02 part of saponin. In making up, add (a) the sodium acetate, (b) the saponin, and (c) the cellulose nitrate, in order to the combined solvents.

(3) For a backing containing a hygroscopic substance, glycerine; an electrolyte, sodium acetate, and a film-former, saponin, the formula, as to ingredients, ranges, and preferred amounts may be the same as for "2," except that it should include in addition approximately 0.25 to 16 parts, preferably 1 part, of glycerine. In preparing, to the combined solvents add (a) the sodium acetate, (b) the glycerine, (c) the saponin, and (d) the cellulose nitrate, in order.

While the various backings may be of any desired thickness serving the ends sought, I have found a relatively thin backing desirable. A film base for them may be "4," sodium acetate omitted.

(4) For a film body, not having a backing but yet containing an electrolyte, sodium acetate, I recommend the following formula:—

	Approximate Range.	Preferred.
Cellulose nitrate (dry).....	25 to 50	35
Sodium acetate.....	0.25 to 10	1
Camphor.....	2 to 6	4
Wood alcohol.....	90 to 150	120
Acetone.....	10 to 50	20
Fusel oil.....	20 to 50	40
Amyl acetate.....	10 to 30	20

15 When making up, add (a) the sodium acetate, and (b) the cellulose nitrate in order, to the combined solvents.

(5) For a similar film body and containing an electrolyte, sodium acetate, and a film former, saponin, the formula, as to ingredients, ranges, and preferred amounts, may be the same as "4" except that it should include, in addition, approximately 0.0125 to 0.3 part, preferably 0.05 part, of saponin. 25 When preparing, to the combined solvents add (a) the sodium acetate, (b) the saponin, and (c) the cellulose nitrate, in order.

(6) For a similar film body containing a hygroscopic substance, glycerine, an electrolyte, sodium acetate, and a film former, saponin, the formula, as to ingredients, ranges, and preferred amounts, may be the same as "5" except that it should include, in addition, approximately 0.5 to 10, preferably 2, parts of glycerine. 35 In making up, to the combined solvents add (a) the sodium acetate, (b) the glycerine, (c) the saponin, and (d) the cellulose nitrate, in order.

40 In all the above formulas the nitrocellulose may have 11½% or less nitrogen content or may have more than 11½% nitrogen content but, as explained above, it is desirable that nitrocellulose having a nitrogen content of 11½% or less, that is, not over 11½% nitrogen content, be used for the backings, and that such backings be applied to a base of cellulose nitrate having more than 11½% nitrogen content. 50 In the cases of unbacked films it is desirable to use cellulose nitrate having more than 11½% nitrogen content.

To provide backings which are soluble in water and can be totally removed, say in development (after which there is no longer any danger from "static marks") glycerine, sodium acetate and saponin in the preferred amounts and ranges given in formulas "1", "2" may be dissolved in 100 to 400, preferably 200, parts of denatured alcohol.

Although, for purposes of specific illustration, I have made more particular reference to cellulose nitrate as the pellicle base to be used for the various layers, it is to be

understood that I do not restrict my invention to the use of cellulose nitrate. I have found that the relations, as regards conductivity, hygroscopicity, and strength, existing between (a) cellulose acetate having more than 55% combined acetic acid and (b) cellulose acetate having 55% or less, that is not over 55%, combined acetic acid, are closely comparable to the relations existing between (a) cellulose nitrate of more than 11½% nitrogen content (b) cellulose nitrate of 11½% or less nitrogen content, the hygroscopicity and conductivity of cellulose acetate decreasing as the percentage of combined acetic acid increases. I have also found that cellulose acetate of either type is well capable of valuable use, with or without the addition of other substances, i. e. a hygroscopic material, an electrolyte, a film former, in ways substantially similar to those discussed above; and a cellulose acetate of low esterification, e. g. not over 55% combined acetic acid, and containing or not containing the said substances, can be used to back a base of nitrocellulose of high esterification, e. g. more than 11½% nitrogen content and, similarly, cellulose nitrate of low esterification, e. g. not over 11½% nitrogen content and containing or not containing the said substances, can be used to back a base of cellulose acetate of high esterification, e. g. more than 55% combined acetic acid; the advantage of increased conductivity being obtained in each case. Also starch acetate, more particularly of the hot-water-soluble type, is more conductive and hygroscopic than the ordinary film and is capable of desirable use, more particularly as a backing, either with or without additional substances of the types mentioned.

While, in describing my invention, I have referred to it as embodied in a "body without a backing" and as embodied in a "backing" it is to be understood that by neither of these terms do I exclude films wherein the pellicle which more particularly exemplifies the invention may have applied to its (normally) exposed surface a coating of such character as not to destroy the efficacy of the pellicle, the pellicle, from the standpoint of the present invention, yet being "without a backing" or being a "backing" as the case may be.

Of course, should it be desired for any reason, both the film base and the backing of a backed film may contain the conductivity-increasing substances.

I claim:

1. A photographic film having a backing containing sodium acetate.
2. A photographic film containing an electrolyte and a film former.
3. A photographic film containing sodium acetate and a film former.

4. A photographic film containing an electrolyte and saponin.
5. A photographic film containing sodium acetate and saponin.
- 5 6. A photographic film containing a hygroscopic substance, an electrolyte and a film former.
7. A photographic film containing glycerine, an electrolyte, and a film former.
- 10 8. A photographic film containing a hygroscopic substance, sodium acetate, and a film former.
9. A photographic film containing a hygroscopic substance, an electrolyte, and saponin.
- 15 10. A photographic film containing a hygroscopic substance, sodium acetate, and saponin.
11. A photographic film containing glycerine, sodium acetate, and a film former.
- 20 12. A photographic film containing glycerine, sodium acetate, and saponin.
13. A photographic film having a cellulose ester base, and a backing containing sodium acetate.
- 25 14. A photographic film having a base and a backing, said backing comprising 4 to 16 parts of a pellicle base and 0.25 to 16 parts of sodium acetate.
- 30 15. A photographic film having a base and a backing, said backing comprising 8 parts of a pellicle base and 1 part of sodium acetate.
- 35 16. A photographic film having a base and a backing, said backing comprising 4 to 16 parts of a pellicle base, an electrolyte, and 0.005 to 0.20 part of saponin.
- 40 17. A photographic film having a base and a backing, said backing comprising 8 parts of a pellicle base, an electrolyte, and 0.02 part of saponin.
- 45 18. A photographic film having a base and a backing, said backing comprising 4 to 16 parts of a pellicle base, 0.25 to 16 parts of glycerine, an electrolyte, and a film former.
- 50 19. A photographic film having a base and a backing, said backing comprising 8 parts of a pellicle base, 1 part of glycerine, an electrolyte, and a film former.
- 55 20. A photographic film having a base and a backing, said backing comprising 4 to 16 parts of a pellicle base, 0.25 to 16 parts of glycerine, 0.25 to 16 parts of sodium acetate, and 0.005 to 0.20 part of saponin.
- 60 21. A photographic film having a base and a backing, said backing comprising 8 parts of a pellicle base, 1 part of glycerine, 1 part of sodium acetate, and 0.02 part of saponin.
22. A photographic film having a base and a backing, the pellicle-forming constituent of said backing having a greater conductivity than said base.
23. A photographic film having a base, and a backing of carbohydrate ester, said ester having a greater hygroscopicity than said base.
24. A photographic film having a base of carbohydrate ester, and a backing also of carbohydrate ester, the ester of said backing having a greater hygroscopicity than the ester of said base.
25. A photographic film having a base of esterified cellulose, and a backing also of esterified cellulose, the esterification of the cellulose of said backing being relatively less than that of the cellulose of said base.
26. A photographic film having a backing of cellulose nitrate having a nitrogen content of not over 11½%.
27. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said backing being of greater hygroscopicity than the cellulose nitrate of said base.
28. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said backing being of lower nitrogen content than the cellulose nitrate of said base.
29. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said base having a nitrogen content of more than 11½%, and the cellulose nitrate of said backing having a lower nitrogen content than has the cellulose nitrate of said base.
30. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said base having a nitrogen content of more than 11½%, and the cellulose nitrate of said backing having a nitrogen content of not over 11½%.
31. A photographic film having a base of low conductivity, relative to that of the hereafter named pellicle-forming constituent of the backing, and a backing the pellicle-forming constituent of which is more conductive than said film base, said backing containing a conductivity-increasing substance.
32. A photographic film having a backing of cellulose nitrate containing a conductivity-increasing substance.
33. A photographic film having a cellulose ester base, and a backing of cellulose nitrate containing a conductivity increasing substance.
34. A photographic film having a backing of cellulose nitrate containing an electrolyte.
35. A photographic film having a cellulose ester base, and a backing of cellulose nitrate containing an electrolyte.
36. A photographic film having a layer of cellulose nitrate having a nitrogen content of not over 11½% and said layer con-

taining a conductivity-increasing substance.

37. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said base having a nitrogen content of more than $11\frac{1}{2}\%$, and the cellulose nitrate of said backing having a nitrogen content of not over $11\frac{1}{2}\%$, said backing containing a conductivity-increasing substance.

38. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said base having a nitrogen content of more than $11\frac{1}{2}\%$ and the cellulose nitrate of said backing having a nitrogen content of not over $11\frac{1}{2}\%$, said backing containing 4 to 16 parts of cellulose nitrate and 0.25 to 16 parts of sodium acetate.

39. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said base having a nitrogen content of more than $11\frac{1}{2}\%$ and the cellulose nitrate of said backing having a nitrogen content of not over $11\frac{1}{2}\%$, said backing containing 8 parts of cellulose nitrate and 1 part of sodium acetate.

40. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said base having a nitrogen content of more than $11\frac{1}{2}\%$ and the cellulose nitrate of said backing having a nitrogen content of not over $11\frac{1}{2}\%$, said backing containing 4 to 16 parts of cellulose nitrate, an electrolyte, and 0.005 to 0.20 part of saponin.

41. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said base having a nitrogen content of more than $11\frac{1}{2}\%$ and the cellulose nitrate of said backing having a nitrogen content of not over $11\frac{1}{2}\%$, said backing containing 8 parts of cellulose ni-

trate, an electrolyte, and 0.02 part of saponin.

42. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said base having a nitrogen content of more than $11\frac{1}{2}\%$ and the cellulose nitrate of said backing having a nitrogen content of not over $11\frac{1}{2}\%$, said backing containing 4 to 16 parts of cellulose nitrate, 0.25 to 16 parts of glycerine, an electrolyte, and a film former.

43. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said base having a nitrogen content of more than $11\frac{1}{2}\%$, and the cellulose nitrate of said backing having a nitrogen content of not over $11\frac{1}{2}\%$, said backing containing 8 parts of cellulose nitrate, 1 part of glycerine, an electrolyte, and a film former.

44. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said base having a nitrogen content of more than $11\frac{1}{2}\%$, and the cellulose nitrate of said backing having a nitrogen content of not over $11\frac{1}{2}\%$, said backing containing 4 to 16 parts of cellulose nitrate, 0.25 to 16 parts of glycerine, 0.25 to 16 parts of sodium acetate, and 0.005 to 0.20 part of saponin.

45. A photographic film having a base and a backing each of cellulose nitrate, the cellulose nitrate of said base having a nitrogen content of more than $11\frac{1}{2}\%$, and the cellulose nitrate of said backing having a nitrogen content of not over $11\frac{1}{2}\%$, said backing containing 8 parts of cellulose nitrate, 1 part of glycerine, 1 part of sodium acetate, and 0.02 part of saponin.

In testimony whereof I affix my signature.

EARLE C. PITMAN.

taining a conductivity-increasing substance.

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trate, an electrolyte, and 0.02 part of saponin.

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EARLE C. PITMAN.

Certificate of Correction.

It is hereby certified that in Letters Patent No. 1,570,076, granted January 19, 1926, upon the application of Earle C. Pitman, of Parlin, New Jersey, for an improvement in "Nonstatic Photographic Films," errors appear in the printed specification requiring correction as follows: Page 2, line 114, for the syllable "hydro-" read *hygro*; page 3, line 59, after the figure "2" insert "and 3"; same page, line 75, after the word "content" insert the word *and*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23d day of February, A. D. 1926.

[SEAL]

WM. A. KINNAN,
Acting Commissioner of Patents.

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