No. 610,861. Patented Sept. 13, 1898.

H. GOODWIN.

PHOTOGRAPHIC PELLICLE AND PROCESS OF PRODUCING SAME.

(Application filed May 2, 1887.)

(No Model.)

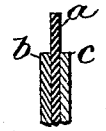
Fig.5. 

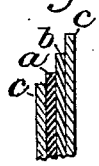
Fig.6. 

Fig.7. 

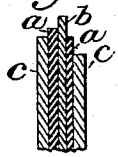
Fig.8. 

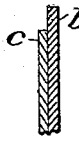
Fig.9. 

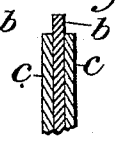
Fig.10. 

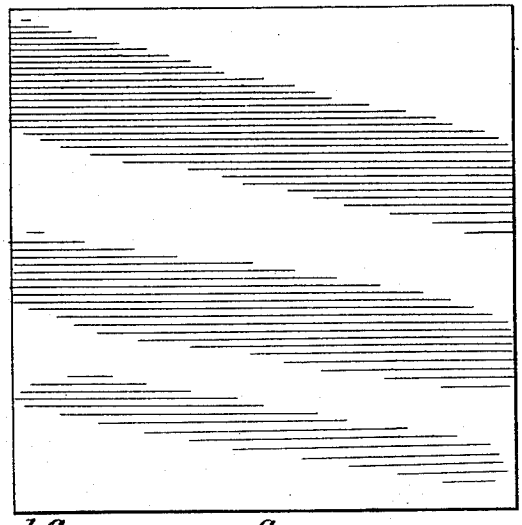
Fig.1. 

Fig.2.

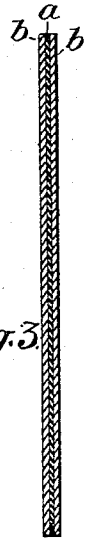


Fig.3.

Fig.4.

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UNITED STATES PATENT OFFICE.

HANNIBAL GOODWIN, OF NEWARK, NEW JERSEY.

PHOTOGRAPHIC PELLICLE AND PROCESS OF PRODUCING SAME.

SPECIFICATION forming part of Letters Patent No. 610,861, dated September 13, 1898.

Application filed May 2, 1887. Serial No. 236,780. (No model.)

To all whom it may concern:

Be it known that I, HANNIBAL GOODWIN, a citizen of the United States, residing at Newark, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Photographic Pellicles and Processes of Producing the Same; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same, reference being had to the accompanying drawings, and to letters of reference marked thereon, which form a part of this specification.

The object of this invention is primarily to provide a transparent sensitive pellicle better adapted for photographic purposes, especially in connection with roller-cameras.

Heretofore for a long period the photographically-sensitive films have been supported by glass plates. These, when carried by tourists or outdoor photographers on their travels, have been a source of much inconvenience because of their weight, bulk, and brittle nature. More recently the sensitive film has been supported upon paper in combination with gelatin and other substances. While this latter avoids the objections involved in the use of the glass, it cannot be advantageously employed under all the various conditions common in photography. For example, the gelatin cannot be brought into contact with heat or water for any considerable length of time without being injured, and it must be made transparent preparatory to the printing process, or it must be stripped from its sensitive film, and the latter must be again secured to a transparent support before the said sensitive film can be used. To avoid these objections and to provide a film having additional qualities in photography, I have provided a pellicle the principal ingredient in the supporting-film of which is nitrocellulose, such as is hereinafter referred to, which after treatment is transparent and insoluble in the usual developing, fixing, and intensifying solutions or liquids used in photography—such, for example, as solutions of alkaline pyro or ferrous oxalate, (developers,) hyposulfite of soda, (fixer,) and bichlorid of mercury, (intensifier.)

I am aware that various attempts have been made to provide a flexible and transparent pellicle having properties common to glass for resisting the action of the fluids above referred to, but so far as I am aware such attempts have been failures from practical photographic and commercial standpoints and have not effected a pellicle capable of resisting the said fluids and having the desired smoothness, hardness, and toughness of surface and capacity and adaptability for service in a roller-camera.

Referring to the accompanying drawings, in which like letters of reference indicate corresponding parts in each of the views, Figure 1 is a plan of a pellicle of the improved composition and arrangements of parts, and Figs. 2 to 10 are sectional views illustrating certain modifications.

The invention consists in the improved pellicle and in the improved process of manufacturing or making the same and in the arrangements and combinations of parts thereof, all substantially as will be hereinafter set forth, and finally embraced in the clauses of the claim.

In carrying out the invention I provide a suitable surface, such as that of glass, and flow over the same a solution of nitrocellulose (by which I do not mean a solution of the compound known as "commercial celluloid" dissolved in alcohol or ether) dissolved in nitrobenzole or other non-hydrous and non-hygroscopic solvents, such as may be employed in producing celluloid, as distinguished from collodion and diluted in alcohol or other hydrous and hygroscopic diluent. The equivalents for nitrobenzole are those non-hydrous non-hygroscopic fluid solvents of nitrocellulose which are non-miscible with water, of slow volatility, and non-greasy, including nitrobenzole, above named, acetate of amyl, &c., which effect, when the solution has been flowed over a smooth plate, a smooth, transparent, imporous, impermeable film capable of being subjected to the photographic fluids above mentioned without being affected thereby. The solution obtained by dissolving the nitrocellulose in said non-hydrous non-hygroscopic solvent is diluted with alcohol or other diluent, which, like alcohol, serves to dilute or expand the volume of the dissolved nitrocellulose and increase its fluidity and which may

be and ordinarily is hygroscopic, miscible with water, and highly volatile. This diluted solution is then applied to a smooth and hard surface, from which it may be stripped when dry.

It would appear after careful investigation that the element of water enters into the drying and hardening operation as a factor for consideration. Officinal alcohol, whether ethylic or methylic, is composed of absolute alcohol and water, the first being a solvent of nitrocellulose when combined with some other solvent. Other solvents of nitrocellulose or diluents of dissolved nitrocellulose—such as ethyl acetate, methyl acetate, and acetone—also contain as a part of their commercial composition a considerable portion of water. Now this water contained in the alcohols, acetone, acetates, and the like does, after the evaporation of the pure alcohol, acetate, or acetone element, act powerfully as a precipitant of dissolved nitrocellulose, and consequently acts as an accelerator in the setting, drying, and hardening of the resulting film. These hydrous and hygroscopic alcohols, acetates, &c., have a lower boiling-point than water, and therefore in evaporating from a solution of nitrocellulose they leave water, which they contain, behind them in the solution, whereas those other non-hydrous and non-hygroscopic elements above described are of a boiling-point higher than that of the water which may have been introduced into the dissolved nitrocellulose, and therefore after the said water, having exercised its accelerating effect upon the precipitation of the nitrocellulose, has itself evaporated from the solution those said non-hydrous and non-hygroscopic elements remain still in a fluid state, with the function of allowing the atoms of nitrocellulose to be held in such a position of equilibrium, contiguity, and contact as finally to combine together in the formation of the desired film. Water, therefore, with a boiling-point of 212° Fahrenheit is a divisional criterion by which one class of slowly-volatile celluloidal solvents (which I may term for purposes of this case "eventual" or "final" solvents, because of their remaining in the solution after the evaporation of the water in the solution, which final solvents are represented by nitrobenzole, with a high boiling-point of about 415° Fahrenheit, and therefore with a relatively slow evaporating quality) may be distinguished from another class of celluloidal solvents or diluents having a low boiling-point and a relatively quick evaporating quality—such, for example, as wood-alcohol—with a boiling-point of 149° and methyl acetate of 133°, &c. These latter solvents, I have discovered, while being celluloidal solvents of nitrocellulose, will not act efficiently as final or eventual solvents, but are valuable as diluents. They are hygroscopic and miscible with water. They evaporate quickly, leaving the water as a precipitant. If there were no eventual celluloidal solvent remaining present until after the evaporation of the water, it is found that the resulting pellicle would be of imperfect transparency and otherwise defective as a pellicle; but while these quick evaporating, hygroscopic, and more or less hydrous solvents may serve useful functions in facilitating the consolidating and drying of the celluloidal film they cannot serve with the best results as eventual solvents under ordinary atmospheric conditions. The eventual celluloidal solvents, such as nitrobenzole and amyl acetate, boiling-point 284°, remaining after the evaporation of the hygroscopic and hydrous elements, being non-hygroscopic and non-hydrous and non-miscible with water and yet fluent, allow the film after the evaporation of the water and hygroscopic matter to remain more or less fluent, so that it is given a full and sufficient opportunity to settle and harden into a compact, clear, and smooth pellicle having the peculiar glass-like but flexible characteristics before recited. Having evaporated the more quickly volatile and hygroscopic fluid matter and the nitrocellulose having had a full opportunity to settle and close the pores from which the more volatile diluent escaped and then having evaporated the less volatile non-hygroscopic fluid instead of a porous, spongy, and weak residual film, a compact, hard, tough, self-supporting, non-porous, and structureless sheet remains, which is flexible to a degree suited to roller-camera purposes, my process admitting of its being made in lengths of indefinite extension and capable of being cut down to a size suitable for the roller-camera roll, but which is, notwithstanding such cutting down, still of a length sufficient to receive a multiplicity of impressions or exposures. This sheet or film is also clearly transparent, smooth, and exceedingly thin as compared with the ordinary glass plates or the plates formed by compression or shaving, the improved pellicle being two one-thousandths of an inch, more or less, in thickness, and thus when in combination with the sensitive films, which may be applied on both sides, sharp lines of light and shade may be secured on the printed pictures; is non-hygroscopic and will not be affected by changes in the atmosphere due to the moisture therein and will not expand or contract or otherwise change its nature by the application of the usual solutions employed in photography; is not of a greasy nature, and thus will not repel the sensitive emulsion, but will admit of smooth and even spreading of the same thereon; one that is devoid of knife marks or streaks and is elastic or is capable of being rolled upon the spools or rollers of the camera, and yet when unrolled will readily extend itself in developing and fixing solutions and be conveniently adapted to lie smooth in the printing operation, &c. It will not fuse under the influence of ordinary strong heat; but by this I do not wish to be understood as saying that it will not ignite

when in contact with a flame. All these qualifications are important in a flexible support or pellicle, and never before have they all been united in one photographic pellicle. The supporting portion of the pellicle being thus formed, I then, either before or after stripping it from the plate or surface on which it has set or dried, coat it by any well-known method of applying such a coating with bromid of silver emulsion or any other sensitive compound or matter capable of being affected photographically.

To reduce the cost of the pellicle having the desired qualities above referred to and yet provide a pellicle having a perfect homogeneity and to prevent the sensitive film from separating from the support forming a part of the pellicle, I may envelop the treated nitrocellulose supporting-film or impose on it a film of gelatin or equivalent transparent matter, or, furthermore, I may coat a layer of gelatin with outer films of the non-hygroscopic nitrocellulose film, so that water or the solvents above referred to cannot gain access to the said gelatin. The gelatin thus imposed on the non-hygroscopic nitrocellulose pellicle is unsensitized, but is substantially a solution of the pure or uncompounded material.

The pellicle of non-hygroscopic nitrocellulose and gelatin prepared as above described formed by successive flowing and drying may be made as follows:

First. I may apply to the glass surface or other temporary support a very thin film of the nitrocellulose compound, and when this is dry I may superimpose upon it a film of gelatin, and when this has been sufficiently dried I may superimpose upon it a very thin film of the same nitrocellulose compound, which when dry may in turn be coated with the photographic mixture.

Second. I may immerse a gelatin film in a solution of the nitrocellulose compound, then hang up the pellicle to dry, and when dry it will be ready to be coated with sensitive mixture. In lieu of the gelatin I may employ any other suitable transparent matter, such as shellac or rosin compounded with albumen.

For some purposes in photography the gelatin may be imposed on but one side of the cellulose film, serving to give increased thickness to said film without materially increasing the cost thereof.

For some purposes in photography I prefer to tint the film, either while the same is being formed or subsequently, with any suitable color, such as that given by iodin.

Referring to the accompanying drawings, illustrating sectional views of the various arrangements of layers which may be employed in producing the sensitive foils whereby it is adapted for various specific purposes, Fig. 2 illustrates an arrangement of films in which *a* indicates a basic film of gelatin. *b b* are films of nitrocellulose compound imposed on opposite sides thereof and protecting the gelatin from the action of the water or other solvent commonly employed in the developing, fixing, and intensifying processes in photography, and *c* is a film of sensitive matter which may be imposed on one or both sides of the transparent flexible support *b b*.

Fig. 3 illustrates the gelatin film coated on opposite sides with the nitrocellulose prepared as described. This forms a pellicle of sufficient thickness to form a stable support for the sensitive matter.

Fig. 4 illustrates a film of nitrocellulose *b* and a film of gelatin *a* or its equivalent, forming a transparent and flexible pellicle which may be also employed in photography. In this case, as in the preceding case, the gelatin may be rendered comparatively insoluble by alum or other chemicals and also rendered more flexible by glycerin.

Fig. 6 illustrates a transparent and flexible pellicle consisting of a film of such matter as dried solution of nitrocellulose *b*, coated on one side with a layer of gelatin *a*, or of calendered and insoluble gelatin, to which is attached a film of sensitive photographic matter, either on one side or on both sides.

In Fig. 7 is illustrated a transparent and flexible film consisting of the prepared nitrocellulose with a layer of insoluble gelatin and also coated on the other side with a layer of insoluble gelatin and both coatings being rendered more flexible by glycerin.

Fig. 8 illustrates a transparent and flexible pellicle consisting of a film of the prepared nitrocellulose coated on both sides with layers of gelatin, which may be calendered or rendered insoluble and more flexible, and finally one or both being coated with a film of sensitized photographic matter.

Fig. 9 represents a transparent and flexible pellicle consisting of a film transparent, insoluble and flexible nitrocellulose prepared as described, coated on one side with a film of suitable photographically-sensitive matter.

In Fig. 10 the film of prepared nitrocellulose is coated on both sides with photographically-sensitive matter. This feature of coating both sides of the transparent film is of peculiar value in that I am enabled to obtain peculiarly effective results in photographing, the double film of sensitive matter giving differences of light and shade and the thinness of the film or the close proximity of the two sensitive films taken together giving in the printing process a stronger picture, with more perfect lines of demarcation between the lights and shades.

Other combinations of films might be specified, each meeting in practice some peculiar want or having a special advantage; but it is deemed unnecessary to further particularize such additional combinations.

After drying in the improved pellicle the fluent solvents and diluents are entirely or almost entirely eliminated from the support, so that the sensitive pellicle when complete

comprises in the pellicle preferred almost, if not entirely, a film of pure transparent nitrocellulose and a photographically-sensitive film. I refer, of course, in the above statement to the pellicle in its simpler form without the additional layers for special purposes above described.

Having thus described the invention, what I claim as new is—

1. An improvement in the art of making transparent flexible, photographic-film pellicles, the same consisting in dissolving nitrocellulose in a menstruum containing a hygroscopic element and an element which is non-hygroscopic, the non-hygroscopic element being of itself a solvent of nitrocellulose, and of slower volatility than the hygroscopic element, depositing and spreading such solution upon a supporting-surface, and allowing it to set and dry and harden by evaporation, and spreading a photographically-sensitive solution on the hardened film, and drying the film, substantially as set forth.

2. An improvement in the art of making transparent, flexible, photographic-film pellicles, the same consisting in dissolving nitrocellulose in a menstruum containing an element whose boiling-point is above that of water as nitrobenzole, and an element whose boiling-point is below that of water as alcohol, the element having the higher boiling-point being of itself a solvent of nitrocellulose, spreading such solution upon a supporting-surface, and allowing it to set and dry and harden by evaporation, and applying photographically-sensitive matter thereto, substantially as set forth.

3. An improvement in the art of making transparent, flexible, photographic-film pellicles, the same consisting in dissolving nitrocellulose in a menstruum containing an element whose rate of volatility is higher than that of water, and an element whose rate of volatility is lower than that of water, the element of lower volatility being non-hygroscopic and itself a solvent, depositing and spreading such solution upon a supporting-surface, and allowing it to set and dry and harden by evaporation, and applying photographically-sensitive matter thereto.

4. An improvement in the art of making transparent flexible, photographic-film pellicles, the same consisting in dissolving nitrocellulose in a menstruum containing elements having, respectively, high and low rates of volatility as compared with water, the elements having low rates of volatility being non-hygroscopic and solvents of nitrocellulose depositing and spreading such solution upon a supporting-surface, and allowing it to set and dry and harden by evaporation, and applying photographically-sensitive matter, substantially as set forth.

5. An improvement in the art of making transparent flexible, photographic-film supports, the same consisting in dissolving nitrocellulose in a menstruum containing an element which is hydrous and an element which is anhydrous, depositing and spreading such solution upon a supporting-surface and allowing it to set and dry and harden by evaporation, and applying photographically-sensitive matter, substantially as set forth.

6. An improvement in the art of making transparent flexible, and elastic photographic pellicles, the same consisting in dissolving nitrocellulose in an eventual celluloidal menstruum which is anhydrous and non-hygroscopic, spreading such solution upon a supporting-surface, allowing it to dry and harden, spreading photographically-sensitive matter, thereon and again drying and stripping the pellicle from said support, substantially as set forth.

7. The process of making photographic pellicles which consists in subjecting nitrocellulose to the action of nitrobenzole, or its non-hygroscopic, non-greasy, cellulodial equivalent, applying the solution to or upon a supporting-surface and drying or setting the same to produce a smooth transparent supporting-film, then imposing upon said film a photographically-sensitive matter, and drying the same into a non-hygroscopic transparent, self-supporting, elastic and flexible photographically-sensitive pellicle, substantially as set forth.

8. The process of making photographic pellicles, which consists in subjecting nitrocellulose to the action of a menstruum combining fast and slow evaporating solvents, the slow evaporating solvent being non-hygroscopic and non-greasy in nature and quality and acting as an eventual solvent as described, spreading the solution upon a support and setting the same by evaporation, then applying photographically-sensitive matter and stripping, all substantially as set forth.

9. As a new article of manufacture, a film-support for photographic purposes, the same consisting of a thin, transparent film, foil, or pellicle of a dried and hardened celluloidal solution of nitrocellulose, said film being coated on one side with a film of gelatin, and having on the other side a coating of photographically-sensitive matter as and for the purposes specified.

10. As a new article of manufacture, a transparent film-support for photographic purposes, the same consisting of a thin, non-greasy, film, foil or pellicle of a dried and hardened celluloidal solution of nitrocellulose, combining in addition to the following essential properties of glass-plate supports, viz., insolubility in developing fluids, insensibility to heat and moisture, imporosity of structure, and hardness, smoothness, and brilliancy of surface, the further desirable properties of exceeding thinness, lightness in weight, toughness in texture and elasticity in flexure; as and for the purposes specified.

11. The improved photographic pellicles, herein described, comprising a clearly and evenly transparent, elastic and dry residual

efluxion, consisting of the evaporated thinly-spread flowage of nitrocellulose dissolved in one of the non-hygroscopic celluloidal solvents and dried, and a film of photographically-sensitive matter, substantially as set forth.

12. The process of manufacturing photographically-sensitive pellicles, consisting of flowing a non-photographically-sensitive solution of nitrocellulose dissolved in a non-hygroscopic liquid, or a liquid which is eventually non-hygroscopic, and drying and hardening such compound into a support for the photographically-sensitive emulsion and imposing on such support the said sensitive emulsion, substantially as set forth.

In testimony that I claim the foregoing I have hereunto set my hand this 29th day of April, 1887.

HANNIBAL GOODWIN.

Witnesses:
CHARLES H. PELL,
OSCAR A. MICHEL.