

# UNITED STATES PATENT OFFICE.

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CASEIN PHOTOGRAPHIC FILM AND PROCESS OF MAKING SAME.

SPECIFICATION forming part of Letters Patent No. 705,643, dated July 29, 1902.

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To all whom it may concern:

Be it known that I, OTTO BUSS, a citizen of the Republic of Switzerland, and a resident of Rüschiikon, near Zurich, Switzerland, have invented new and useful Improvements in Casein Photographic Films and Processes of Making the Same, of which the following is a specification.

Many attempts have been made to utilize the vegetable and animal albuminoids classed under the name of "caseins" as photographic layers either for positive printing or for the negative process. Thus in various publications descriptions have appeared of processes for manufacturing such layers—as, for instance, in Halleur's *Kunst der Photographie*, (Art of Photography,) 1853; Martin's *Handbuch der Photographie*, (Manual of Photography,) 1857, page 214; Hartwich's *Manual of Photographic Chemistry*, 1863, page 194; *Photograph Archives*, 1873, page 142; *Photographische Correspondenz*, 1873, page 127; *Photographic News*, 1884, page 12; *Photographisches Wochenblatt*, (Photograph Weekly Journal,) 1884, page 66; in German Patent No. 95,548, and elsewhere. The layers made according to these processes consist, in consequence of their mode of manufacture, one and all of the silver compounds necessary for the production of the picture—such as silver bromid, iodid, chlorid, citrate, tartrate, &c.—and of a silver compound of the casein. In all the processes in question the silver compounds are made by means of an excess of silver nitrate to form solutions or layers consisting of metallic compounds of the caseins and metallic compounds of haloid acids. In each case the integral part of the layer active in the production of the picture consists of silver salts of casein and not of free caseins. As the casein-silver compounds, serving in that case both as carrier of the picture and as the material to produce the picture, would be injured by the fixing agents used in photography, it is not possible to attain a sufficient resistance of the layers without the addition of hardening mediums to counteract the influences of the photographic coloring, fixing, and washing processes.

The photographic casein layers produced by me differ entirely from those made accord-

ing to the above-mentioned processes, since they consist of insoluble free caseins as picture-carriers and contain the silver compounds necessary for the production of the picture without the addition of silver caseinate. These new layers are the result of observing the fact that caseins which have been reduced to solution by organic or inorganic acids and water are precipitated in an insoluble form by metallic-salt solutions free from silver—such as haloids, sulfates, phosphates, nitrates, &c.—and that insoluble casein layers made accordingly can be impregnated afterward with salt solutions. By an appropriate choice of such solutions any silver compound necessary for the production of the picture—such as the chlorid, iodid, bromid, citrate, phosphate, tartrate, benzoate, &c.—can be incorporated into the mass of casein either directly or by double decomposition.

The solutions of caseins in aqueous solutions of the above-mentioned acids have the property of coagulating in the cold, so that with these solutions, just as easily as with gelatin solutions, papers, films, plates, &c., of any material can be lightly coated in thin layers and afterward be made insoluble by a certain treatment with the aforesaid salt solutions. The layers obtained consist of free caseins, are not, therefore, to be converted by silver-salt solutions into silver caseinate, are insoluble in ordinary neutral solvents, and yet are pervious to water and salt solutions, also offer resistance like leather, and can be kept smooth by an addition of glycerin or similar substances.

For the production of printing-out paper the following proportions are used: Five hundred to seven hundred grams of pure dry milk casein are placed in nine liters of water and the mixture heated to from 35° to 50° centigrade. Then two hundred and fifty grams of citric acid dissolved in one liter of water are added thereto. The casein in further heating dissolves to an easily-flowing clear liquid that will on cooling to about 9° to 15° centigrade become hardened into a stiff gelatinous mass similar to solutions of glue. To the above clear solution are added one hundred to two hundred cubic centimeters of glycerin and the whole filtered while warm. Ordinary

paper or baryta photographic paper is then coated with the filtrate while warm (35° to 40° centigrade, for example) by means of the usual machines employed for the purpose and in a manner similar to glue solutions, after which the paper is cooled and the coating becomes hard. The paper is then dried, and a brilliant smooth flexible sheet is obtained, the film on which is, however, still easily soluble in water. The dried paper is then slowly drawn through or floated with coated side down on a solution containing from five per cent. to seven per cent. of ammonium chlorid or sodium chlorid until the film or coating is well soaked with the solution. This treatment renders the casein film insoluble in water. There remains in the film sufficient citric acid so that in the subsequent treatment with silver nitrate the silver chlorid and silver citrate will be both formed in proper proportions. The quantities of silver citrate and chlorid formed in the film can be regulated by suitably varying the quantity of citric acid used in dissolving the casein and by varying the concentration of the chlorid-bath. In place of citric acid any other suitable organic or inorganic acid may be used, such as lactic acid, benzoic acid, acetic acid, tartaric acid, phosphoric acid, &c. The dry or still damp paper is now made sensitive by means of a silver-nitrate solution in the same manner as albumen-paper, in which the paper is cut into sheets and floated upon a solution containing four per cent. to twelve per cent. of silver nitrate, or if the paper is to be made in rolls, the usual machines for coating the surface may be used, in which the paper is drawn over the surface of the solution. The superfluous silver-nitrate solution is wiped off the surface of the paper, and the paper is then dried.

By the suitable selection of chlorids or mixtures of such as toning-bath for the film, as well as the acids or mixtures of acids for the solution of the casein, the greatest variations in sensitiveness, color, and depth or brilliancy of the picture can be obtained. If a fixing-bath is used of an iodine or bromine salt or a mixture of both, with or without the addition of a chlorine salt, it is possible to produce a silver-bromid or silver-iodid paper or a silver-iodid-bromid paper with or without silver chlorid, said paper containing varying quantities of silver chlorid and resembling the gelatin papers.

Films of casein can be made upon any carrier or basal material for their support, as glass, celluloid, gelatin, mica, leather, silk, wood, &c.

It is self-evident that any kind of silver compound suitable for photographic negative and positive processes can be incorporated into such layers or any combinations of such silver compounds or combinations of silver compounds with other bodies—as, for in-

stance, sensitizers, as coloring-matters, alkaloids, glycosids, &c. It is also self-evident that by an appropriate choice and by a series of dipping-baths used for the production of the sensitive substance in the film layers can be produced suited for every kind of process, either for a negative process with silver bromid, silver chlorid, or silver iodid, &c., or for positive processes with silver chlorid, silver bromid and chlorid, or silver bromid alone for developing by means of silver haloids precipitated by the action of excess of halogen or for printing out in combination with silver phosphate, tartrate, citrate, &c. In all these cases the formation of silver caseinate does not take place, since the layer is made of casein in its free state.

The new layers or films described are especially adapted for the photographic copying-out process with silver chlorid, and they produce printing-paper of most excellent quality. They copy easily and rapidly in agreeable tones, they tone easily and regularly, and produce soft harmonious pictures of uncommon beauty. At the same time these papers are unusually capable of resisting mechanical injury both in a dry and wet condition, and they lie in the baths perfectly flat and smooth, and the temperature of the baths has no deleterious effect on their solidity.

Having thus described my invention, what I claim as new therein, and desire to secure by Letters Patent, is—

1. The process of producing actinic films, which consists in forming a solution of casein, coating a suitable support therewith, rendering the casein film substantially insoluble and then sensitizing the film, substantially as described.

2. The process of producing actinic films, which consists in forming a solution of casein, coating a suitable support therewith, rendering the casein substantially insoluble by a solution of a metallic salt free from silver, and then sensitizing the coating, substantially as described.

3. The process of producing actinic films, which consists in forming a solution of casein, adding thereto a softening agent, coating a suitable support therewith, rendering the casein substantially insoluble, and then sensitizing the coating, substantially as described.

4. The process of producing actinic films, which consists in producing a solution of casein with an organic acid, adding thereto glycerin, coating a suitable support therewith, rendering the casein substantially insoluble by means of a solution of a haloid salt free from silver, and then sensitizing the coating, substantially as described.

5. An actinic layer for photographic purposes, consisting of free casein and a sensitizing medium, substantially as and for the purpose set forth.

6. An actinic layer for photographic pur-

poses consisting of free casein rendered substantially insoluble and a sensitizing medium, substantially as and for the purpose set forth.

5 7. An actinic layer for photographic purposes consisting of substantially insoluble free casein, a softening agent and a sensitizing medium, substantially as described.

8. An actinic layer for photographic purposes consisting of substantially insoluble

free casein, glycerin and a sensitizing medium, substantially as described.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

OTTO BUSS.

Witnesses:

A. W. BAUER,  
ANDRÉ HAR.