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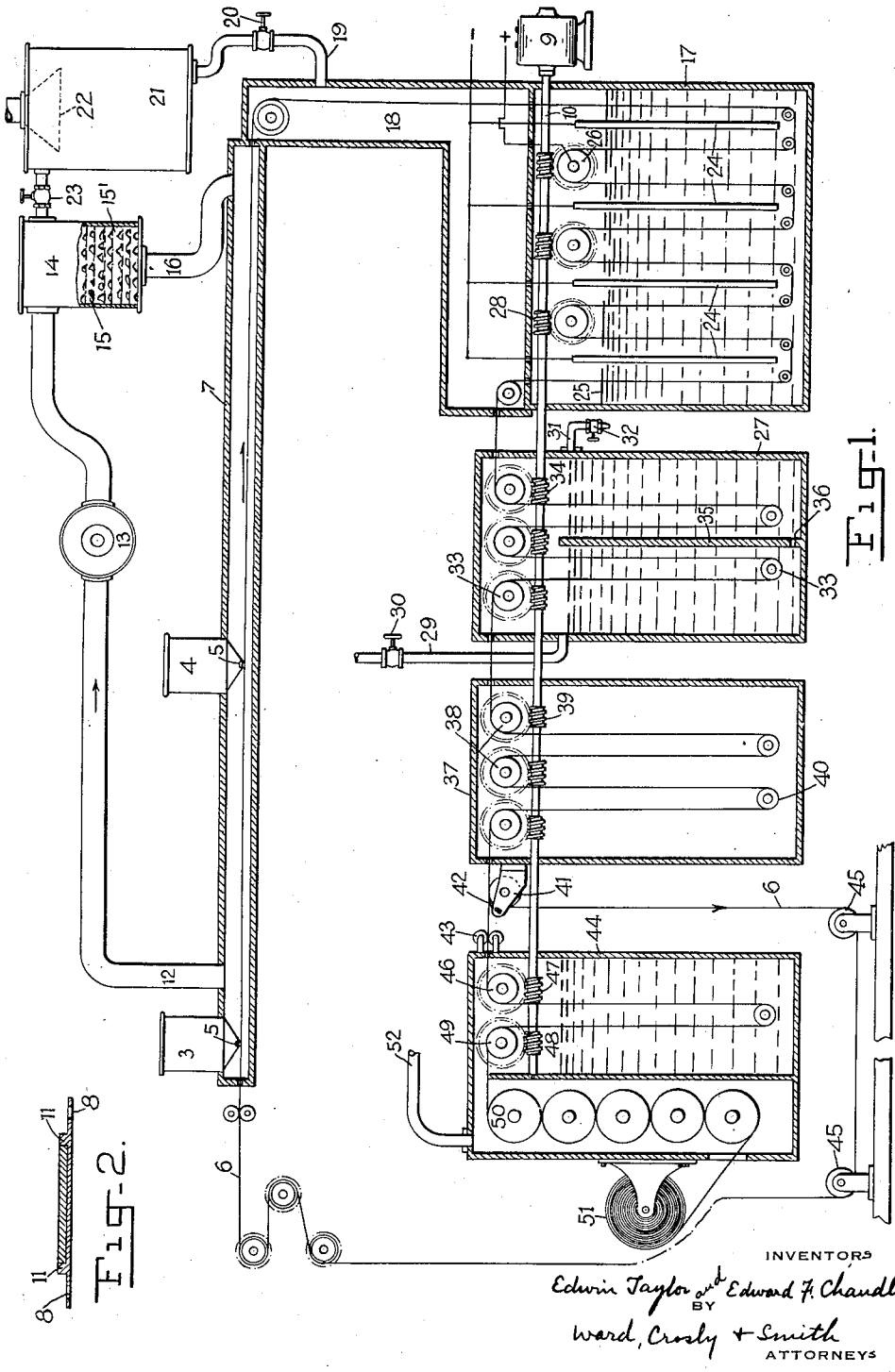


Fig-1.

Fig-2.

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PHOTOGRAPHIC FILM AND METHOD OF MAKING THE SAME.

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The invention relates to improvements in photographic films and methods of making the same. The main object of the invention is to provide a photographic film from which flaking off or scratching off of the sensitized or photographic salt or salts is substantially prevented and at the same time provide a strong and durable film. A further object is to provide a simple, efficient and economical film and method of producing the same. Further and more specific objects, features and advantages will more clearly appear from the detail description given below taken in connection with the accompanying sheet of drawings which form a part of this specification. This application is a continuation in part of our prior application Serial No. 341,953, filed December 2, 1919.

In the drawings we have illustrated a suitable apparatus for forming a cellulosic film to be impregnated with a suitable photographic salt or salts. In said drawings Fig. 1 illustrates in vertical cross-section, parts being broken away, the arrangement of a suitable plant for manufacturing photographic films, and Fig. 2 is an enlarged cross-sectional detail of the endless belt and film formed thereon.

In the preferred method of forming the film fibrous or cellular cellulose material is dissolved in a suitable solvent such as cupro-ammonia solution, and this is filtered to remove impurities and the solution concentrated by the partial removal of ammonia and water (as for instance by means of a vacuum or suction). The resulting homogeneous fluid is flowed on a carrier which may be a flexible band of metal suitable for employment as one of the elements of an electrolytic cell, the said carrier being adapted to convey the flowed material through preferably a dry and inert gas, thereby excluding deleterious atmospheric contamination. The carrier conveying the flowed material now enters and becomes preferably one of the elements or electrodes, in a bath which may be provided with another element or electrode, so as to constitute an electrolytic cell upon the energization of the said elements and through which the carrier which may be the anode, is adapted to continuously convey to the flowed material. Owing to the electrolytic characteristics of cellulose in a colloidal state, the flowed material as it passes through the influence of the said electric field or fields is converted from the colloidal solution to a solid or more dense state, which transformation should be completed under proper conditions of time and current density before the carrier and material leaves the cell. During the period of transformation the volatile constituent is released from the mass and is in a condition to be conveyed to a suitable condensing or recovering system, the metallic constituent being deposited on the cathode in recoverable condition. The transformed organic material free of all traces of any ingredient that might cause future deterioration is preferably conveyed through a suitable washing system where any adhering or extraneous traces of foreign materials are removed and thence to a suitable drying system for the removal of any moisture content after which the converted material is ready for separation from the conveyer or carrier. This separation may be effected by means of a V-shaped fixed edge supplemented by two rolls.

The resultant material is a transparent flexible band resembling celluloid in appearance. It may be treated with a volatile solvent such as amyl acetate to increase its surface lustre, density, etc., for certain purposes, or at once impregnated with a suitable photographic salt or salts, as hereinafter described.

Referring to the drawings, 3—4 indicate suitable tanks carrying concentrated solution of cupro-ammonia or concentrated solution of zinc chloride both being good solvents for cotton which may be used in the manufacture of the film. About one pound of cotton may be used to about twenty pounds of the solution and suitable means such as the valve 5 may be provided for regulating the flow of the material upon the endless belt 6 which passes entirely through the closed tray or chamber 7 as shown.

The belt may be made of copper and may be platinum plated and buffed and may be suitably perforated as indicated at 8 in Fig. 2 to receive the teeth of sprocket wheels for driving the same, suitable means for

driving the belt being provided such as 9, an electric motor connected to the driving shaft 10. Upon the belt may be provided suitable strips of material such as 11 between which the flowing material from the tanks 3—4 is deposited. In the drawing we have illustrated the belt as traveling from left to right looking at Fig. 1.

The ammonia from the closed tray 7 is drawn through the outlet pipe 12 by the suction fan 13 and is passed through the drying chamber 14 provided with suitable grids 15 upon which lime or other suitable material 15' may be piled, the dry ammonia returning through the pipe 16 into the closed tray 7 as shown. This provides a constant circulation of dry ammonia gas in the closed chamber 7 and prevents waste of material and contamination from the outside.

17 indicates an electrolytic cell to be hereafter more fully referred to and is in communication with the superimposed chamber 18 through which ammonia, hydrogen, oxygen or other gases rise and escape by way of the pipe 19 controlled by the valve 20 into the chamber 21 escaping under the hood 22 for condensation and recovery except when the valve 23 is open to allow the same to pass to the drying chamber 14.

The electrolytic cell 17 may be provided with copper electrodes 24 or when the process is worked with zinc chloride, zinc electrodes may be used. An acidulated solution of nitric or sulphuric acid 25 is provided as an electrolyte sufficiently strong to carry the current.

As the cellulose fed upon the belt 6 passes down through the chamber 18, it passes beneath the first electrode 24 at the right side of the figure over the pulley 26, beneath the next electrode, over the next pulley and so on until it enters the chamber 27, said pulleys being driven by the worms 28 upon the motor shaft 10 and said electrodes being connected to the negative side of a suitable source of electricity as shown, with the result that the metallic content of the cellulose upon the belt is electrodeposited therefrom upon the electrodes 24 leaving the cellulose gradually becoming white instead of blue as it passes through the electrolytic bath until upon leaving said bath the cellulose is quite white, whereupon it enters the washing tank 27 before referred to. The film is now sufficiently tough and flexible for washing whereas if the metallic content remained in the film, it would upon drying be brittle and liable to break up. In the washing tank 27 water enters by the pipe 29 controlled by the valve 30 and escapes by the pipe 31 which may be provided with a valve 32, the film passing over the pulleys 33 driven by the worms 34 upon the said motor shaft 10, and a suitable partition 35 may be provided with an opening at the bottom as indicated at 36 so as to bring the film in contact with the cleaner water of the wash as it leaves the tank 27. All of these tanks are preferably closed to prevent foreign matter from coming in contact with the film and if desired suitable means may be provided for evacuating air therefrom as any carbonic acid present in the room is apt to form carbonate. This especially applies to the drying tank, and various other objectionable results may be encountered. The washing tank removes any adhering ammonia, acid, or particles of matter, after which the film passes to the drying chamber 37 where it again passes over pulleys such as 38 driven by worms such as 39 and beneath pulleys such as 40 until it finally emerges over the pulley 41 as shown. This drying tank may of course, be heated by any suitable means to a temperature, say perhaps 120 degrees Fahrenheit. The film is now loosened from the belt upon which it was formed and due to the heat, shrinkage, etc., is readily separated therefrom, and in this connection a suitable knife or stripper such as 42 may be provided adjacent the periphery of the roll 41 so as to allow the film to pass leftwardly between the rollers 43 of the tank 44 while the belt or carrier passes downwardly beneath the pulleys 45 from which point it returns to the starting place and again passes through the closed tray 7. Should it be desired to treat the cellulose film with amyl acetate the detached film is caused to enter the tank 44 in which it passes over the roller 46 driven by the worm 47 and downwardly through the amyl acetate bath 48 passing upwardly again over the roller 49 and upon the rolls 50 preferably of highly polished surface. In the amyl acetate tank the film is softened, densified, and is increased in its resistance to moisture, after which, upon passing first leftwardly around the top roll 50, then rightwardly around the next roll below, and leftwardly again, and so on alternately, it becomes thoroughly dried and finished and is wound upon the reel 51, while the amyl acetate vapors escaping through the outlet 52 may be condensed for re-use, thus providing a continuous, economic, and practical method of producing film in which there are practically no losses, but complete recovery of materials, the film being adapted to travel through the system with a speed of production higher than in any of the present well known methods, while at the same time producing a film of greater transparency and durability, one which is practically non-combustible and of numerous other properties and advantages.

To sensitize the film for photographic purposes we preferably impregnate it from one side (preferably uncalendered) with a solution of a photographic salt such as a

solution of a suitable silver salt. This may be a sensitive silver salt, but we prefer to impregnate the film with a solution of nitrate of silver. This may be done by flowing a solution of the salt over the surface of the film in the usual way. After impregnating the film with the silver nitrate solution the film may be exposed to an atmosphere of, and impregnated with bromine, chlorine, iodine, or a combination thereof, thereby depositing insoluble bromide or chloride, etc., of silver in the film itself. That is, the halogen will automatically permeate the solution which has already permeated substantially the entire body of the film, and thereby cause a deposition of photo-sensitive silver salt throughout substantially the entire film. By preparing photographic films in this manner, after the same has been photographically exposed and developed, there is no flaking off or scratching off of the negative surface, thus preventing the objectionable effects in photography so much complained of, as even if the surface of our film be scratched or mutilated, the chemicals having penetrated the film, still present the photographic image, which in the path of the light registers the characters, notwithstanding the mutilated surface of the film.

The cupro-ammonia solution hereinbefore referred to is preferably made by dissolving hydrated cupric-oxide CuH_2O_2 in approximately an equal weight of ammonia water containing thirty per cent (30%) ammonia hydrate NH_4OH. The resulting solution is of an intensely blue color and may be considered to be merely a mixture of cupric-oxide, (CuO) ammonia (NH_3) and water. We have found even under adverse conditions that with about two amperes per square inch of anode, that we can obtain about forty grams of cellulose and about twenty-three and one-half grams of copper in about an hour and a half. This however is not submitted as an accurate statement as to what may be done under more favorable conditions.

Another method of producing our improved film is as follows: We protect one side of the film by means of a coating of paraffine or by close contact with a revolving drum, and while thus protected to pass the film slowly and continuously through any desired nitrating bath of nitric and sulphuric acid. By this means the surface exposed to the acid is nitrated to any desired depth, the depth of nitrating being controlled by the speed of the film or by the degree of concentration of the acid mixture. The film is now passed through a water bath, the protective coating stripped or otherwise removed (when used) and the film is passed through an electric field between electrodes immersed in a dilute alkaline solution by which means the last traces of acid are readily removed or decomposed. The film is again washed in hot running water and may be dried on hot rolls. It is now passed through a volatile solvent such as acetone or amyl acetate, the non-nitrated side being protected by a drum and the nitrated side gelatinized to the full depth of nitration. The film is now drawn through a drying chamber and the volatile solvent removed. At this stage the product consists of a tough cellulose-like, waterproof backing gradually merging into a non-nitrated water-absorbing facing. The facing is now impregnated with any desired light-sensitive salts, passed through boiling water to improve the sensitiveness if desired and finally dried. All of the above operations are continuous.

The product obtained by these operations compares more than favorably with the present celluloid films. It is cheaper to manufacture and the cost of plant is much less. It is very much slower burning, and is not explosive as practically half of it is un-nitrated and the fact that the light-sensitive material, silver for instance, is deposited directly in the film itself instead of being merely coated on the outside, effectually prevents scratching or peeling off with the consequent production of light streaks, etc., upon the projection on a screen. The silver deposited being of a considerable depth, approximately .002 of an inch in place of only .0004 of an inch as in present films, permits of a scratch five times as deep as with the present films, and a correspondingly increase of life of the film. Tracing, blue-print material, etc., made of this material are superior and cost but little more. They are oil and moisture-proof, are transparent and may be printed one from another quite readily.

While we have described our improvements in great detail and with respect to preferred embodiments thereof, we do not desire to be limited to such details or embodiments, since many changes and modifications may be made and the invention embodied in widely different forms without departing from the spirit and scope thereof in its broader aspects. Hence we desire to cover all forms coming within the language or spirit of any one or more of the appended claims.

What we claim as new and desire to secure by Letters Patent, is:

1. A sensitive transparent cellulose film for photographic purposes, essentially characterized by the fact that the entire film is impregnated with a sensitive salt of silver.

2. A transparent cellulosic film having a photographic salt deposited in the body thereof.

3. A transparent photographic film hav-

ing a sensitive photographic salt deposited in the body thereof.

4. A photographic film comprising a transparent body of cellulose with a sensitive photographic compound situated substantially throughout the body of the film.

5. A transparent photographic film comprising a body of cellulosic material substantially the entire body portion of which is impregnated with a sensitive photographic compound.

6. A transparent film comprising a toughened surface on one side and a sensitive salts carrying surface on the other side.

7. A film composed of cellulosic material having a layer of toughened cellulosic material on one side and a sensitive salts carrying layer on the other side.

8. The method of making photographic film which consists in electrolytically depositing cellulose and impregnating a transparent film thereof with a sensitive photographic compound.

9. The method of making photographic film which consists in impregnating a film of transparent cellulosic material with a photographic compound.

10. The method of making photographic film which consists in impregnating a transparent film of cellulose with a sensitive photographic compound.

11. The method of making photographic film which consists in impregnating a transparent film of cellulosic material with a silver salt, and treating the film with a halogen to deposit the silver halogen salt in the body of the film.

In testimony whereof we have signed our names to this specification.

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