

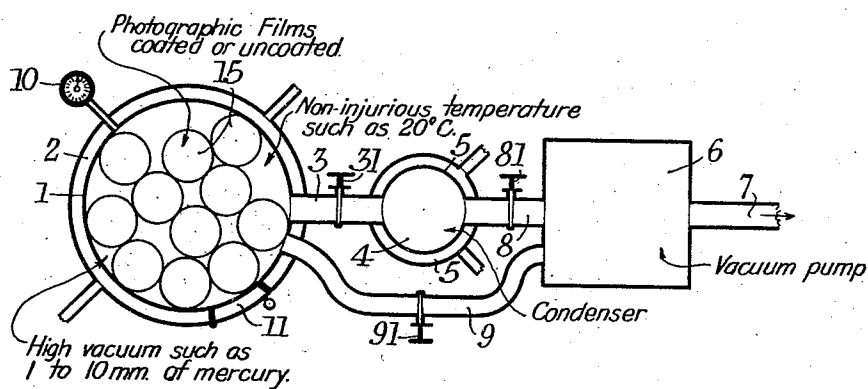
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PROCESS OF CONDITIONING PHOTOGRAPHIC FILMS

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PROCESS OF CONDITIONING PHOTOGRAPHIC FILMS

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This invention relates to processes of conditioning photographic film. One object of the invention is to provide a conditioning process which will improve both coated film having a light-sensitive photographic layer and uncoated film before it is covered with such a layer. Another object is to provide a process for preshrinking coated or uncoated film so that its subsequent shrinking will be usefully reduced. Still a further object is to provide a process for conditioning film having a light-sensitive photographic layer so that the time during which said layer will keep unimpaired or unfogged will be greatly increased. Another object is to provide a relatively simple and inexpensive process which will improve some of the desirable properties of even highly sensitive photographic films, such as dye-backed motion picture films, without injuring them in any respect. Other objects will hereinafter appear.

In the accompanying drawing is shown a diagrammatic plan view of one form of apparatus in which my process can be carried out.

Uncoated films for photographic purposes comprise chiefly flexible, transparent, water-resistant colloided cellulose compounds, such as esters and ethers, the commonest being cellulose nitrate, cellulose acetate and ethyl cellulose. These cellulosic compounds have also associated with them, in most cases, a colloided organic substance of low volatility which acts as a softener or plastifier to impart flexibility and other qualities to the film.

In the preparation of such film, both the cellulosic compound and the softener are dissolved in a volatile solvent, by which term I include, for convenience, not only true individual solvents, but mixtures of such solvents with volatile liquids, which have no solvent properties by themselves. The solutions thus prepared are spread or shaped into films on polished surfaces and the volatile ingredients are allowed to evaporate until the films become strong and can be stripped from said surfaces. The films are then subjected to heat and currents of drying gases, which remove further portions of the volatile

solvents from the film and "cure" it. Among the very large number of film compositions which might be cited, typical ones will be found in U. S. Patents Nos. 1,342,601, Seel, June 8th, 1920; 1,342,602, Seel, June 8th, 1920, and 1,583,709, Webb, May 4th, 1926.

Films thus prepared are coated with light-sensitive photographic layers, such as gelatino-silver-halid emulsions, the customary precautions being taken to make the emulsion adhere to the cellulosic base. All of such coated films eventually have to pass through photographic developing, fixing and washing baths and then are dried. Moreover, those films which are made into positive motion pictures are afterwards subjected to heat conditions during projection and are stored for considerable periods. The result is that such films shrink some in said photographic manipulations and then progressively during storage and use. At the end of a year, for example, there is a very considerable shrinkage resulting from both treatment and length of use.

This is objectionable, because the shrinking alters the relative locations of the sprocket holes in motion picture film and interferes with the proper passage of the film through the apparatus, occasioning consequent rapid deterioration.

Sprockets which fit the freshly perforated films will not properly fit films which have shrunk for a considerable period, say a year. Conversely, sprockets which fit old shrunk films do not fit fresh film well. Since a lack of fit rapidly wears the film, it is highly desirable to treat the film so that its cooperation with a sprocket will average well during use, say during the first year. In other words, the length of such film during the year should deviate very little from the average length for that period, thus causing minimum wear.

While I have not been able to fully reach the desired results, nevertheless, I have found that a very useful advance toward them can be obtained by preshrinking the film through removal of quantities of volatile solvent that would normally remain therein when the film reached the purchaser.

This removal of residual volatile solvents can be successfully accomplished from coated or uncoated films.

When my process is applied to coated photographic films, I have also found that it greatly increases the time during which the light-sensitive layer will keep in good condition without spoiling or fogging. This sensitive layer is usually, and preferably, a gelatino-silver-halid emulsion containing moisture, the latter being present in an amount corresponding to the humidity of the atmosphere in which the coated film was dried. The chemical processes which take place during the spoiling or fogging of such a layer depend upon the presence of this small amount of moisture. It is an advantage of my process that it removes enough of this moisture to practically inhibit the progress of such harmful processes.

In film manufacture it is often desirable to manipulate coated films under higher humidity than is good for permanently conditioning said films. My process enables the excess moisture in the films, absorbed during such humid manipulations, to be safely removed.

The removal of both the bulk of the residuum of volatile solvent and of the moisture from the coated film cannot be effected by ordinary drying operations at atmospheric pressure with heat, because this injures the film and the coating. I have found that the conditioning of the film, so as to effect preshrinking and stabilization of the emulsion, can be carried out by submitting the film to a high vacuum under temperature conditions which do not injure the film or coating. While some coated films can, for example, be safely treated under a vacuum of 150 millimeters of mercury at 60° C., I prefer to maintain the film at approximately room temperature (of the order of 20° C.) and under these conditions I prefer to employ a vacuum below 10 millimeters (say .25 millimeters, for example) of mercury. The pressure in the vacuum is at least as low as the vapor pressure of water at the temperature used. This is kept up until the evolution of the solvent residuum and the water from the coating ceases or becomes negligible. This time varies in accordance with the kind of vacuum apparatus, the thickness of the film, the tightness with which it is coiled, the presence or kind of wrappers or containers for it, etc. Seven hours is typical, but it can vary considerably without harm. Operating at such safe temperatures, a vacuum of the degree used in canning operations or even a vacuum of 200 millimeters is useless to accomplish such removal of both the residuum and moisture, even after operating for very much longer, and commercially unpractical periods.

When working with such a relatively high

vacuum, I prefer to condense at least part of the evolved vapors, the temperature of condensation regulating the limit of the vacuum in accordance with well known physical laws. When coated film is treated, it is desirable to freeze the condensed moisture in order to regulate the partial pressure of the solvent and water vapors in the vacuum space, say by cooling the condenser between 10° C. and -70° C. It might be expected that the removal of this moisture would cause an undesirable brittleness in the light-sensitive or emulsion layer. But experience has shown that when the treated film is taken out for use by the consumer, and rehumidified by simple operations, it quickly regains its flexibility. For example, it regains flexibility upon rewinding in a humid atmosphere, or by simply standing in coiled condition exposed to such atmosphere for a few days before use. Thus the increased keeping qualities are not obtained at the expense of permanently impairing the mechanical properties of the film.

The following instances will illustrate how my process may be applied to the conditioning of films at different stages of their manufacture. In the first place it may be applied to the completed films while they are in their wrappers, such as cans, paper, foil, or boxes. See also packages suitable for treatment in U. S. Patent No. 1,377,156, J. G. Jones, May 3, 1921, wrapped article. It has been found that the relatively high vacuum, which I employ, is rapidly effective in removing the residuum of solvent and the moisture even through such ordinary coverings in which the final films are transported or sold; in spite of the fact that such wrappings at atmospheric pressure protect the films in moist climates against the entrance of moisture. Motion picture film cans may have the customary sealing adhesive tape removed or even the cover off during evacuating, but the cans are immediately sealed at the end of the treatment in the usual way with cover and tape. It will be noted that the packaged goods, when the vacuum treatment stops, come back to atmospheric pressure and a vacuum does not persist in the packages.

My process in the second place is convenient as a factory proposition in treating the coated film before it is packed. For example, I can preshrink motion picture film before it is slit and perforated. Thus there is obtained initially an accuracy of perforation-sized and spacing which is close to the average during the first year of use.

In the third place, I can also preshrink the uncoated film after it is cured by the conventional methods and before the emulsion is applied to it.

Referring to the accompanying drawing, 1 designates the conventional showing of a

vessel capable of withstanding atmospheric pressure and remaining tight under the high vacuum which I employ. This is provided with a door 11 which is equipped with the usual gaskets, etc. for preventing leaks. Vessel 1 is also provided with a gauge 10 which may be any suitable type for registering the degree of vacuum which is used. This vessel 1 can be employed at room temperature and in many instances no temperature regulating device is necessary; but it is sometimes convenient to provide a jacket 2 through which a temperature regulating fluid may be circulated, to insure uniformity.

The vessel 1 is connected with the vacuum pump 6 through two alternative paths. The first one is a direct path through pipe 9 controlled by valve 91. The second is through pipe 3 and condenser 4 and pipe 8. Pipe 3 is controlled by valve 31 and pipe 8 by valve 81. The condenser may be of any suitable type in which the temperature can be regulated. In the present example the condenser is provided with a jacket 5 through which the cold brine circulates to give a temperature range from 10° C. to -70° C. The exit 7 from the vacuum pump may lead to the atmosphere or to supplementary condensing or solvent recovery apparatus (not shown).

In operation the films 15 to be treated (herein illustrated for convenience as rolls) are loaded into the vessel 1 and the door 11 tightly closed. If the vessel 1 and the films are not at the desired temperature, they can be brought to it by circulating the controlling fluid in the jacket 2,—say water at 20° C.

With the vacuum pump 6 in operation, valve 91 closed and valves 31 and 81 open, the evacuating of the vessel 1 and films therein takes place with condenser 4 connected into the system, the latter being, for instance, at a temperature of -8° C. or -9° C. The water vapor will condense and be frozen in the condenser. When the water is substantially removed from the film, there will be no further need of condenser 4, and it can be cut out by opening valve 91 and closing valves 31 and 81 and the vacuum treatment continued to insure removal of the bulk of said residuum of solvent. So long as moisture is present, the limit to which the vacuum may be carried depends upon the temperature of the condenser, and thus it can be adjusted accurately by changing such temperature, assuming the vacuum pump to be of adequate power.

Under these conditions I prefer to regulate the vacuum to about .25 millimeters of mercury, between .1 millimeter and 10 millimeters being the most effective range for coated film when the film is at room temperature in vessel 1. If the temperature in vessel 1 is lowered, a higher degree of vacuum and a lower temperature in condenser 4 are used. If, on the other hand, the tem-

perature in vessel 1 is raised somewhat above room temperature, (but always below a temperature which will spoil either the coated or uncoated film) the degree of vacuum need not be quite as high and the temperature in condenser 4 may be raised. But in any event, a relatively high order of vacuum of the kind indicated is desirable.

Even when rolls of coated film are treated, the vapors are removed, by my process, from the inner parts of such rolls. The partial pressures of the volatile solvents are much smaller than the partial pressure of the water vapor. As the latter vapor is drawn over into condenser 4, it carries along the smaller amounts of volatile solvent vapors, thus acting as a sort of scavenger or carrier for the latter and hastening the process.

When the above described process is applied to films having a dye layer of the kind described in my Patent No. 1,638,577, August 9th, 1927, roll film cartridge, it has a still further advantage. It sets or hardens the said dye layer so as to further insure that the latter does not offset or stick to the sensitive emulsion layer with which it contacts in the rolls or cartridges. My process makes certain that there is not enough volatile solvent left in the film to soften the dye layer, even under severe climatic conditions.

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

1. In the process of conditioning film having at least a layer of colloidized cellulosic compound, said layer containing residual volatile solvent, the step of submitting said film to a vacuum to remove solvent, said film being maintained at a temperature at which it remains unimpaired during said removal, and the pressure in said vacuum being at least as low as the vapor pressure of water at said temperature.

2. In the process of conditioning film having at least a layer of colloidized cellulosic compound, said layer containing a residuum of a solvent of high volatility and a plastifier of low volatility, the step of submitting said film to a vacuum to remove solvent, said film being kept at a temperature below 60° C. and said vacuum being less than 150 millimeters of mercury.

3. In the process of conditioning film having at least a layer of colloidized cellulosic compound, said layer containing a residuum of volatilizable solvent, the step of submitting said film to a vacuum to remove solvent, said film being maintained at a temperature at which it remains unimpaired during said removal, at least part of the evolved vapors being condensed at a temperature below 0° C. and the vacuum being regulated by the temperature of such condensation.

4. In the process of conditioning film having at least a supporting layer of colloidized

cellulosic compound and a layer of gelatino-silver-halid photographic emulsion, said first-named layer containing a residuum of volatilizable solvent, and said emulsion containing volatilizable liquid, the step of submitting said film to a vacuum to remove solvent and liquid, said film being maintained at a temperature at which said emulsion remains unimpaired, and the pressure in said vacuum being at least as low as the vapor pressure of water at said temperature.

5. In the process of conditioning film having at least a supporting layer of colloided cellulosic compound, and a layer of gelatino-silver-halid photographic emulsion, said first-named layer containing a plastifier of low volatility and a residuum of a solvent of high volatility, and said emulsion containing moisture, the step of submitting said film to a vacuum until shrunken by removal of solvent and said moisture, said film during said removal being maintained at a temperature of the order of 20° C. and said vacuum being below 10 millimeters of mercury.

6. In the process of conditioning film having at least a supporting layer of colloided cellulosic compound and a gelatino-silver-halid photographic emulsion, said first-named layer containing a residuum of volatilizable solvent, and said emulsion containing moisture, the step of submitting said film to a vacuum until shrunken by removal of solvent and moisture, said film being maintained at a temperature at which said emulsion remains unimpaired, at least part of the evolved vapors being condensed and the vacuum being regulated by the temperature of such condensation.

7. In the process of conditioning film having at least a supporting layer of colloided cellulosic compound and a gelatino-silver-halid photographic emulsion, said first-named layer containing a residuum of a solvent of high volatility and a plastifier of low volatility, and said emulsion containing moisture, the step of submitting said film to a vacuum to shrink it by removal of solvent and moisture, said film being maintained at a temperature at which said emulsion remains unimpaired, the water vapor, thus evolved, being condensed and frozen to regulate the partial pressure of the vapors present in said vacuum.

8. In the process of conditioning film having a layer of colloided cellulosic compound containing a residuum of volatilizable solvent, said layer being coated on one face with a light-sensitive photographic emulsion, and on its other face with a dye layer capable of being softened by said solvent, the step of submitting said film to a vacuum to shrink said film and harden said dye layer by removal of solvent, said film being maintained at a temperature at which said emulsion remains unimpaired.

9. In the process of conditioning packages of photographic film having at least a supporting layer of colloided cellulosic compound containing a residuum of volatilizable solvent and a light-sensitive photographic layer containing moisture, the wrappings of said packages being permeable to moisture vapor when the packages are under vacuum, the step of submitting said packages to a vacuum to remove solvent and moisture, said packages being maintained at a temperature at which the contained film remains unimpaired during said step, said wrapping being resistant to passage of moisture vapor when the packages are at atmospheric pressure.

10. In the process of conditioning film having a layer of colloided cellulosic compound containing a residuum of volatilizable solvent, said layer being coated on one face with a gelatino-silver-halid layer containing moisture and on its other face with a dye layer capable of being softened by said solvent, the step of submitting said film at a temperature of the order of 20° C. to a vacuum of less than 10 millimeters of mercury until solvent and moisture are removed.

11. A conditioned photographic film comprising a layer of colloided cellulosic compound prepared with a volatile solvent and capable of retaining a residuum of said solvent, and a light-sensitive photographic colloid layer capable of retaining moisture, said first-named layer being reduced in volatile solvent content to make it preshrunk with respect to a like layer containing said residuum of said volatile solvent, and said last-named layer being reduced in moisture content to make it keep unfogged longer than a like layer containing more moisture.

12. A conditioned photographic motion picture film comprising a layer of colloided cellulosic compound prepared with a volatile solvent and capable of retaining a residuum of said solvent, a layer of light-sensitive gelatino-silver-halid emulsion thereon capable of retaining moisture, and a backing layer of dye capable of being rendered soft by said solvent, said first-named layer being reduced in volatile solvent content to make it preshrunk relative to a like layer containing said residuum of volatile solvent and to free it from softening effect on said dye layer, said emulsion being reduced in moisture content to make it keep unfogged longer than a like layer containing more moisture.

Signed at Rochester, New York, this 26 day of January, 1928.

KENNETH C. D. HICKMAN.