Fig. 2

Fig. 3

Fig. 4

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This invention relates to a process of preparing photographic film and paper which involves passing a gelatin-silica photographic emulsion preliminarily through a vertical agitated falling film type evaporator and immediately coating out the concentrated photographic emulsion thus obtained onto a support therefor using an extrusion coating operation.

In the usual procedures for preparing photographic products a coating is to photographic emulsion having a considerable content of water is applied to the support. The emulsion layer resulting is ordinarily subjected to a setting effect immediately at coating, such as by chilling or by ammonia fuming as taught in U.S. Patent No. 2,652,345 of J. E. Jones. The latter procedure depends upon the presence of fungicide or some material having similar properties in the photographic emulsion. After setting, the emulsion coating is dried by conditioned air which removes a considerable amount of water therefrom to obtain the final product.

One object of our invention is to provide a method of preparing photographic products in which the emulsion layer immediately solidifies upon application to the support therefor which makes for high speed operations. Another object of our invention is to provide a method for concentrating gelatin-silica halide emulsions which will not alter the photographic properties of the emulsion in the concentrating operation. A further object of our invention is to provide a procedure for concentrating photographic emulsions regulated by controls which are motivated by a device which senses the liquid level in the outlet of the concentrating apparatus. A further object of our invention is to provide a procedure for preparing emulsion coated products wherein the setting of the emulsion upon its application to the support thereafter is simplified, eliminating the necessity of setting sections which have been provided in previous coating operations. A still further object of our invention is to assure uniformity in the application of an emulsion layer to a support in making photographic films and papers. Other objects of our invention will appear herein.

We have found that photographic products may be obtained without many of the difficulties involved in previous procedures for their manufacture by the combination of an extrusion coating operation and a compatible procedure in which the gelatin emulsion is passed through a thin film evaporator by which a considerable proportion of the water therein is removed from the emulsion which is obtained in a heated fluid condition. This heated concentrated emulsion is passed to the hopper of the coating apparatus from which a ribbon of the coating composition is applied to the support. The coating operation is of the extrusion type as described in U.S. Patent No. 2,681,294 of Albert E. Beguin, which in operating in accordance with our invention can be used with or without differential pressure. By adapting this coating method to the preliminary treatment of the emulsion herein described coating speeds are greatly enhanced and immediate setting of the coating when deposed upon the support occurs as a result of decrease of the emulsion temperature.

Our invention can be better understood by describing the apparatus in which the emulsion is treated in preparation for the coating operation.
tor is connected through a valve to a gear pump which pumps the emulsion at a uniform rate into the apparatus. The concentrated emulsion is withdrawn through pipe 16 which is fitted with a pressure level sensing device shown in more detail in FIGURE 3. This instrument is connected to a differential pressure transmitter which regulates steam supply to the jacket of the evaporator so as to control the operation. That the emulsion is not being sufficiently concentrated would be shown by a rise in the level of the liquid in the outlet 16. This is determined automatically by the sensing device which in that case would increase the amount of steam supplied to the evaporator. If, on the other hand, the emulsion is being concentrated to too great an extent a fall in level is detected and the amount of steam introduced is automatically decreased.

In the operation of the arrangement illustrated in FIGURE 2, both the gear pump supplying the emulsion feed to the evaporator and the gear pump withdrawing the concentrated emulsion from the evaporator are run at constant rates which rates are maintained in constant ratio, one to the other. The ratio of the rates at which these gear pumps operate is governed by the concentration of emulsion which has been selected for the evaporator to deliver and the pump rates are set to correspond to that concentration. This rate is arrived at by the actual operation of the evaporating system, but once the rate has been determined the pump is run at that constant rate throughout the operation as is to the pump supplying the emulsion feed to the evaporator.

The emulsion supply gear pump is set at a rate to supply the correct quantity of solids for the coating width and speed to be used. The gear pump withdrawing the concentrated emulsion is set at a rate so that the degree of concentration obtained gives the desired coating properties in the fluid. This concentration is arrived at by coating experience; the withdrawing gear pump rate can then be calculated from the knowledge of feed concentration and pumping rate and desired concentration for coating.

FIGURE 3 is a sectional view of the pressure level sensing device which is attached to the outlet of the evaporator. Any change in the level of the liquid in the outlet tube changes the position of the diaphragm of the sensing device, notice of which is sent to the differential pressure transmitter to which this sensory device is attached. One tube of the sensing device is attached to the high pressure side of the differential pressure transmitter and the outlet tube to the low pressure side of the transmitter and to the top of the evaporator whereby it is under the vacuum at which the evaporator is operated. The position of the diaphragm determines the amount of flow through the nozzle of the sensing device which activates the differential pressure transmitter. The differential pressure transmitter is a well known measuring instrument, marketed by various instrument companies such as Tabor Instrument Company of Rochester, New York. Since in the sensing device the output pressure change is only on the order of a fraction of an inch of water, it is desirable for control purposes to convert this narrow absolute range to a gauge range of 3-15 p.s.i. Therefore, the sensory output and the evaporator vacuum are connected to the pressure differential transmitter which is adjusted to give the 3-15 p.s.i. output for the liquid level range desired.

FIGURE 4 is a block diagram showing the control system by which the intake of steam is regulated. The differential pressure transmitter activates a steam controller which varies the introduction of steam to the jacket surrounding the lower part of the evaporator. When the level of liquid in the outlet tube lowers, the emulsion is being concentrated to too great an extent which calls for a decrease in the flow of steam. Upon lowering of the liquid level the diaphragm of the liquid level sensor recedes from the nozzle opening and a greater flow of air occurs. If, on the other hand, the liquid level rises, the concentration of emulsion is not proceeding to the extent desired. The rise of liquid level is shown by decrease in the flow of air through the sensor which decrease is picked up by the pressure differential transmitter. The steam controller causes an increase in the flow of steam to the steam jacket governed by the rise of the liquid level in the outlet tube. The emulsion is concentrated in the evaporator to a composition containing 30-60% solids which concentrated emulsion is withdrawn from the concentrator by means of a gear pump and then concentrated emulsion is transmitted through a jacketed tube (not shown) to the hopper of an extrusion type coating apparatus.

The temperature of the concentrated emulsion as it is transmitted to the coating apparatus may be kept at or near that at which it comes from the concentrator or it may be allowed to lose some heat providing that the temperature is maintained above the setting or "string-forming" temperature range of the concentrated emulsion. This setting or string-forming temperature may be 20 or more degrees below the temperature of the emulsion as it comes from the concentrator. In practice, it is ordinarily desirable to keep the temperature of the emulsion drop some prior to coating as it is usually an advantage if the coating can be made with the emulsion at a higher viscosity than that which the emulsion should have for best operation of the concentrator. It is a feature of our invention that the concentrated emulsion is not allowed to lose any temperature in transit prior to coating as it is usually advantageous if the coating can be made at a higher viscosity than that which the emulsion should have for best operation of the concentrator.

In operation, the emulsion is fed at a controlled rate into the feed inlet 14 of the evaporator. This emulsion is uniformly distributed by the rotation of the rotor upon the inner wall and the evaporator and flows by gravity to the bottom thereof. The emulsion is subjected in the evaporator to heat and vacuum and the water vapor and non-condensible gases are drawn out through the vapor outlet. The foam which forms when emulsions are subjected to this treatment is mechanically broken in the separation section and falls back as a liquid. The rotor thus serves both as a foam breaker and a means of mechanically agitating the film in the heating section to promote heat transfer.

In the concentrating of photographic emulsions in accordance with our invention it has been found that the use of vacuum within the evaporator and the use of mercury and steam temperatures of 170-265°F. are satisfactory. It has been found that photographic emulsions can be concentrated such as from 10% solids to 50% solids in a very short time such as 30 seconds or less by this method without any overlapping occurring. If the photographic emulsion to be applied to a support has unusual hardening characteristics so that difficulties would be encountered in concentrating it, it is desirable in that case to withhold the hardening agent from the emulsion while being concentrated, and introduce the hardener into the emulsion just before coating or as a layer upon the emulsion coat at the time of coating.

The emulsion after concentration and while still warm is led to the hopper of an apparatus shown in FIGURE 1 of U.S. Patent No. 2,681,294, and from there through the slot directly to the film base or paper base which is coated by the procedure employed there, with or without the differential pressure. The concentrated emulsion which is at an elevated temperature is cooled by contact with the support and because of the lowered water content thereof solidifies immediately upon coating. The photographic material thus obtained needs only treatment for a short time with conditioned air to remove the remaining moisture from the emulsion. It is possible to make the emulsion under darkened conditions to retain the photosensitive characteristics.

The following examples illustrate the preparation of photographic products in accordance with our invention.
Example 1

A coating 4 inches wide of a concentrated gelatin silver halide emulsion is to be made at 100 ft. per minute to give a coverage of 0.415 lb. of dry solids per 100 sq. ft. This is equal to a rate of 0.138 lb. of dry solids per minute. A gelatin silver halide photographic emulsion having a solids content of 12% was pumped by means of a positive displacement gear pump with a variable speed drive at the exact rate of 1.15 lb. per minute to an agitated film evaporator, as described herein, having 1 sq. ft. of heating surface. This rate of feed of the dilute solution carries the exact amount of solids to supply the required coverage of 0.415 lb. per 100 sq. ft. Steam is supplied to the evaporator at a temperature of 249° F., which temperature is controlled by regulation of the steam pressure. The pressure in the evaporator is reduced to approximately 1.94 lb. per sq. inch absolute pressure, which corresponds to a vapor temperature of 125° F., by means of an ejector or other suitable vacuum source.

The rotor blades in the evaporator were operated at a linear speed of 2090 ft. per minute with a clearance between the ends of the blades and the heating surface of \( \frac{1}{4} \) in which operation spread the emulsion on the heating surface of the evaporator in the form of a thin agitated film. Because the temperature of the heating surface is well above the equilibrium vapor temperature, the emulsion boils as it falls by gravity down the walls of the evaporator. The water so vaporized is carried out of the evaporator through a suitable condenser and subsequently removed, together with any non-condensable gases by means of the ejector or other vacuum source. The emulsion flowing down the walls becomes more concentrated until it leaves the heating surface and collects in the discharge line of the evaporator at the bottom. At the end of the discharge line the emulsion flows through a multiport valve to an accurately controlled positive displacement gear pump known as the product pump. The multiport valve is also connected to a wash pump for cleaning purposes. The product pump speed is set to discharge at the exact rate at which the product is concentrated. The temperature and pressure were selected to produce a concentration of 39% solids in the product and therefor the product pump rate was 0.354 lb. per minute. To insure maintaining the 39% concentration the level of the concentrate in the discharge pipe from the evaporator was accurately sensed by a pressure level sensing device which controls the temperature of the steam in the evaporator jacket. Thus, if a deposit accumulates on the evaporator walls and therefore reduces the product concentration, the level tends to rise in the discharge pipe since both feed and product pumps operate at constant volume. This is sensed by the level control which in turn raises the steam temperature, thereby maintaining the desired concentration. In the beginning of the operation the level sensing device may be so connected as to regulate the product pump speed. The concentrated emulsion was pumped directly from the product pump through a water jacketed tube to an extrusion hopper mounted on a coating machine of the type shown in FIGURE 1 of U.S. Patent No. 2,681,294. The emulsion coating was applied to paper base to immediately form an emulsion layer thereon which set upon contact with the paper without any penetration into the fibers thereof. The moisture was removed from the emulsion layer by the use of a current of warm dry air in the conventional manner. Photographic paper was obtained having a smooth coating of the desired weight on the paper.

Example 2

A coating of a gelatin-silver halide photographic emulsion 36 inches wide was desired at the rate of 80 ft. per minute and with a dry solids content of .339 lb. per 100 sq. ft. A gelatin-silver halide photographic emulsion having a solids content of 9.50% was used. The emulsion was pumped from a holding kettle to the evaporator by means of two gear pumps operating in parallel from a common variable speed drive, two pumps being used instead of one to permit operating at low speeds and therefore reduce wear and maintain accuracy. The pumps were driven at such a speed as to accurately deliver 4.28 lbs. per minute each or a total of 8.56 lbs. per minute of emulsion containing .813 lb. per minute of dry solids. The evaporator to which the pumps direct the emulsion was of the agitated film type having 18 sq. ft. of heating surface with a bladed rotor turning at a peripheral speed of 2090 ft. per minute. The steam jacket of the evaporator was divided into 2 parts and the upper and lower halves of the jacket were maintained at different temperatures. The upper jacket was supplied with steam at 194° F. and lower jacket was supplied with steam at 260° F., the steam being obtained from the higher pressure source through reducing valves to the two separate steam jackets. The emulsion entered the top of the heat transfer section of the evaporator and was spread in a thin film on the inner wall of the evaporator section by the action of the rotor blades. The pressure in the evaporator is maintained at approximately 1.94 lbs. per square inch absolute pressure, which corresponds with a vapor temperature of 125° F., this reduced pressure being maintained by means of a steam jacket. The emulsion upon the walls of the evaporator gave up water vapor as it flowed down the wall to be collected in the discharge pipe. The water vapor obtained was carried out of the evaporator through a suitable condenser and was removed together with any non-condensable gases by the ejector.

The discharge pipe of the evaporator was connected to a suitable pump and the concentrated emulsion was removed from the evaporator to the inlet of a variable speed driven gear pump, known as the product metering pump. The constant pressure at the inlet of the product metering pump is obtained by providing a discharge pump with considerably higher capacity and arranging about it a recirculating line, the volume recirculating being controlled by a pressure sensing device at the inlet of the metering pump which controls the regulating valve in the recirculating line. The speed of the metering pump was set to deliver exactly 2.70 lbs. per minute of concentrated emulsion which is the quantity of a 30.5% solution containing .813 lb. per minute of dry solids. This concentration was selected on the basis of previous experience having shown that it would have the required coating properties. The concentrated emulsion was forced through a water jacketed tube through an extrusion type hopper mounted on a coating machine. The coating operation was carried out as described in U.S. Patent No. 2,681,294, cellulose triacetate film base being coated in this operation.

The following table gives the range of conditions used in concentrating 1 type of gelatin-silver halide photographic emulsion in accordance with our invention.

<table>
<thead>
<tr>
<th>Feed concentration</th>
<th>12% solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. used:</td>
<td></td>
</tr>
<tr>
<td>(1) Percent solids</td>
<td>18-45%</td>
</tr>
<tr>
<td>(2) Visc., cp., at 105° F.</td>
<td>200-5000</td>
</tr>
<tr>
<td>Evaporator pressure, p.s.i.a.</td>
<td>1.4-2.0</td>
</tr>
<tr>
<td>Vapor temperature, ° F.</td>
<td>110-125</td>
</tr>
<tr>
<td>Steam temperature, ° F.</td>
<td>2 jackets—180-270</td>
</tr>
<tr>
<td>Product density, gm./ml.</td>
<td>1.12-1.28</td>
</tr>
<tr>
<td>Conc. ratio (usual)</td>
<td>3.25-3.50</td>
</tr>
</tbody>
</table>

In another case a different type of photosensitive silver halide emulsion was concentrated in an agitated film evaporator. The solids concentration in this type emul-
sion was greater than that previously concentrated. The conditions used there were as follows:

Feed concentration 15.3% solids.
Conc. used:

(1) Percent solids 55–60%.
(2) Visc., cp., at 105°F 2500–5000.
Evaporator pressure, ps.i.a. 1.4–2.0.
Vapor temperature, °F. 110–125.
Steam temperature, °F. 2 jackets—180–270.
Product density, gm./ml. 1.49–1.53.
Conc. ratio (usual) 3.75–4.00.

The useful range of pressures in concentrating the emulsion within the evaporator are found within the range of 114–5 lbs. per sq. inch absolute and the useful steam temperatures are found within the range of 150 °F–280 °F. The feed solutions may vary from as little as 2 or 3% solids up to as high as 25% solids and the emulsion concentrations may range anywhere from 25–65% solids or higher depending on the composition of the material and how highly concentrated they must be in order to obtain good coatability.

In some cases it may be desirable to pass the emulsion a second time through the concentrating apparatus to obtain the desired concentration. For instance, in the case of some feed solutions which contain 8% or less of solids and a concentration of 30–60% solids in the emulsion is desirable to obtain good coatability, it might be necessary to run the emulsion through twice. For continuous operation this is most conveniently accomplished by using 2 evaporators in series or a single evaporator which recycles a large proportion of discharge back to the evaporator.

The concentrated emulsion as it comes from the evaporator will have a temperature within the range of 85–130 °F, and the emulsion is maintained at that temperature in transferring it from the evaporator through a jacketed tube maintained at 85–130 °F. to the hopper of the extrusion coating device. The concentrated emulsion has a viscosity of at least 1000 cps. (usually 2000–5000 cps.) at this temperature. When the emulsion having this temperature and viscosity is applied to the support in the extrusion coating operation the emulsion layer forms apparently due to the lowering of the temperature upon exposure to the support and to the air and to the concentration of the emulsion. The emulsion cools to be flowable at room temperature and at temperatures within the range of 85–130 °F. the concentrated emulsion is of such viscosity that only a pressure considerably above that contributed by gravity causes flow of the emulsion.

We claim as our invention:

1. A process of preparing photographic products which comprises passing a gelatin-silver halide photographic emulsion having a solids content within the range of 5–15% through an agitated falling-film type evaporator whereby an emulsion is obtained having a solids content within the range of 30–60% and a temperature within the range of 85–130 °F., transferring the concentrated emulsion to the hopper of an extrusion coating device while substantially maintaining its temperature and extruding the emulsion as a layer upon a support for the emulsion, all under darkened conditions, whereby a photosensitive photographic product is obtained.

2. A process for preparing photographic paper which comprises passing a gelatin-silver halide photographic emulsion having a solids content of approximately 12% through an agitated falling-film type evaporator whereby an emulsion is obtained having a 33% solids content and a temperature of 85–130 °F., transferring the concentrated emulsion to the hopper of an extrusion coating apparatus while substantially maintaining its temperature and extruding the emulsion as a layer upon a paper base, all under darkened conditions, whereby a photosensitive photographic paper is obtained.

3. A process for preparing photographic film which comprises passing a gelatin-silver halide photographic emulsion having a solids content of approximately 9.5% through an agitated falling-film type evaporator whereby an emulsion is obtained having 25–65% solids and a temperature within the range of 85–130 °F., transferring the concentrated emulsion to the hopper of an extrusion coating apparatus while substantially maintaining its temperature and extruding it onto film base, all under darkened conditions, whereby a photosensitive film base is obtained.

4. A process of preparing photographic products which comprises passing a gelatin-silver halide photographic emulsion of 5–15% solids content through a vertical agitated falling-film type evaporator whereby water is driven off and an emulsion is obtained having a solids content of 30–60% and a temperature within the range of 85–130 °F., transferring the concentrated emulsion to the hopper of an extrusion coating device while maintaining its temperature above that at which solidification occurs from which device the emulsion is extruded upon a support for the emulsion, all under darkened conditions, whereby a photosensitive photographic product is obtained.

5. A process of preparing photographic products which comprises subjecting a gelatin-silver halide photographic emulsion having a solids content within the range of 5–15%, while in the form of an agitated film to an elevated temperature whereby an emulsion having a solids content within the range of 30–60% and a temperature within the range of 85–130 °F. is obtained, transferring the concentrated emulsion while substantially maintaining its temperature to the hopper of an extrusion coating apparatus and extruding the emulsion as a layer upon a support therefor, all under darkened conditions whereby a photosensitive photographic product is obtained.

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