United States Patent [19]

Greiller

[11] **3,867,901**

[45] **Feb. 25, 1975**

[54] **APPARATUS FOR PRODUCTION OF PHOTOGRAPHIC ELEMENTS**

[75] Inventor: **Jack F. Greiller,** Ruislip, England

[73] Assignee: **Eastman Kodak Company,** Rochester, N.Y.

[22] Filed: **Sept. 22, 1972**

[21] Appl. No.: **291,440**

Related U.S. Application Data

[60] Continuation of Ser. No. 24,457, March 16, 1970, abandoned, which is a division of Ser. No. 733,944, June 3, 1968, Pat. No. 3,632,374.

[52] **U.S. Cl.** **118/50,** 118/301, 118/325, 118/DIG. 4

[51] **Int. Cl.** **B05c 5/00**

[58] **Field of Search** 118/DIG. 4, 301, 324, 325, 118/24, 50, 6, 412; 53/140; 117/105.3

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3,205,089	9/1965	Kinzelman	118/DIG. 4
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Primary Examiner—John P. McIntosh
Attorney, Agent, or Firm—W. F. Delaney

[57] **ABSTRACT**

In the manufacture of photographic elements, such as photographic film or paper, apparatus for coating the support by forming a free-falling vertical curtain of liquid photographic coating composition in such manner that the curtain is stable and has a uniform flow rate across its width and directing the support so that the free-falling curtain impinges thereon, while maintaining a controlled relation between the flow rate and the speed at which the support is moved, to form a thin layer of the coating composition on the face of the support. Such apparatus includes means for advancing the support at the desired speed and a hopper for the coating composition which is provided with a downwardly inclined slide surface down which the coating composition flows by gravity, the slide surface terminating in a lip spaced vertically above the moving support from which the coating composition flows as a free-falling curtain.

8 Claims, 16 Drawing Figures

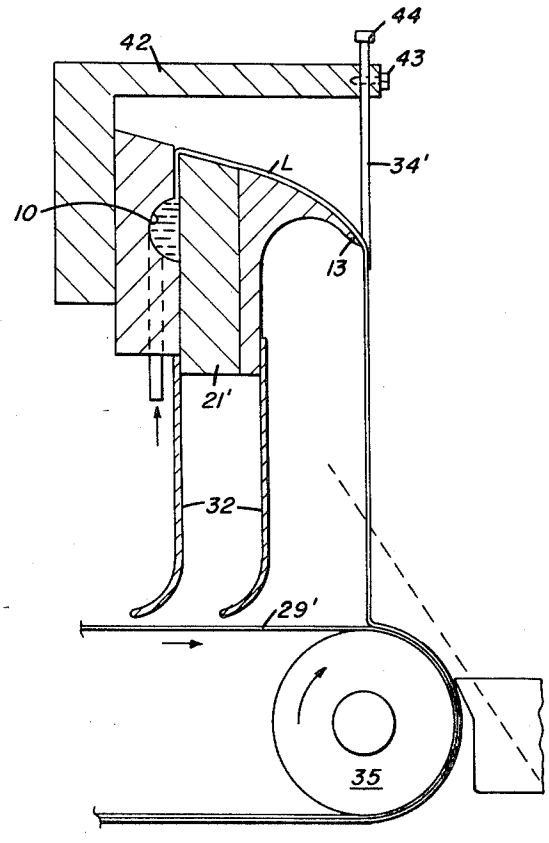


FIG. 1

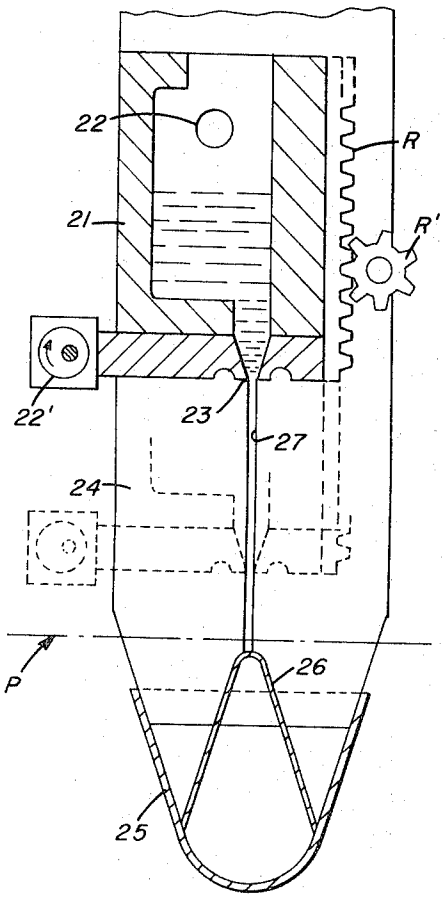


FIG. 2

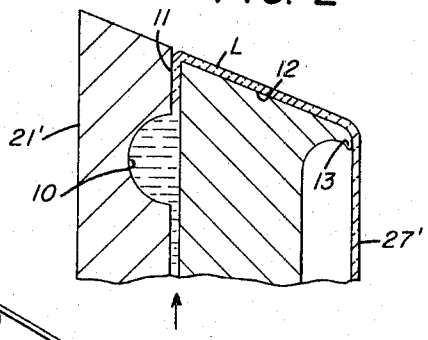


FIG. 3

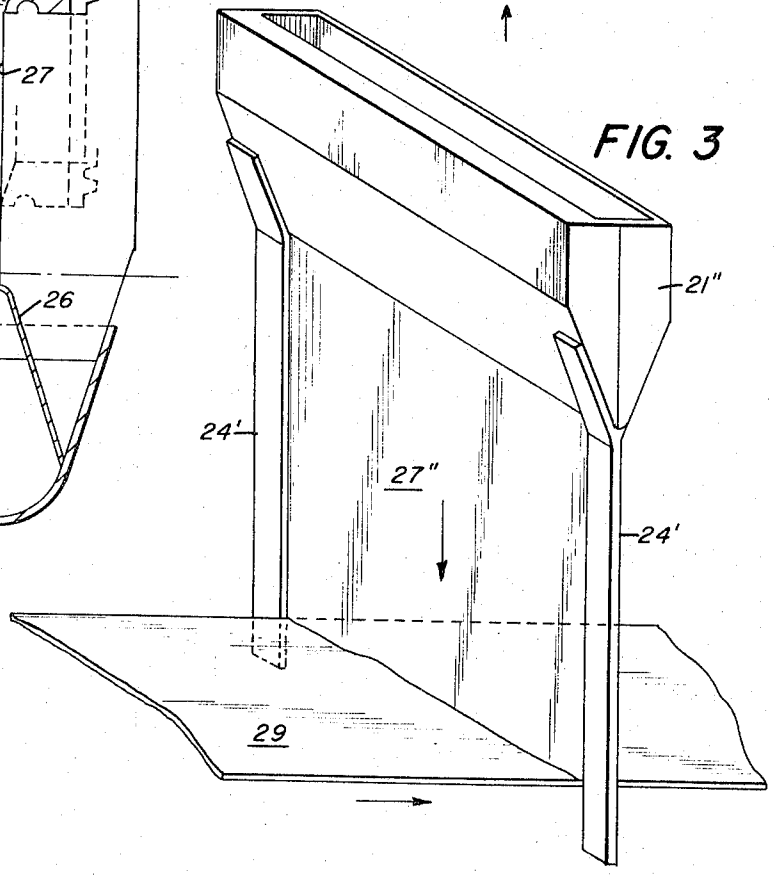


FIG. 4

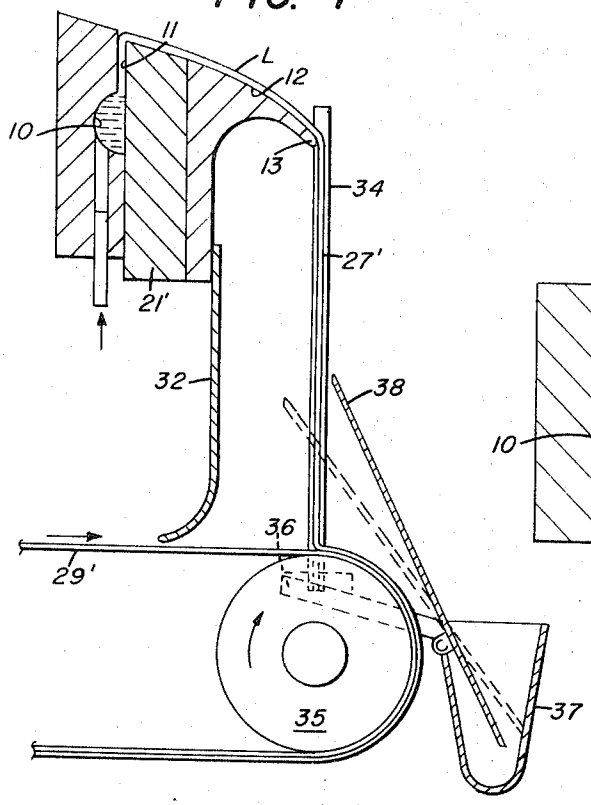


FIG. 6

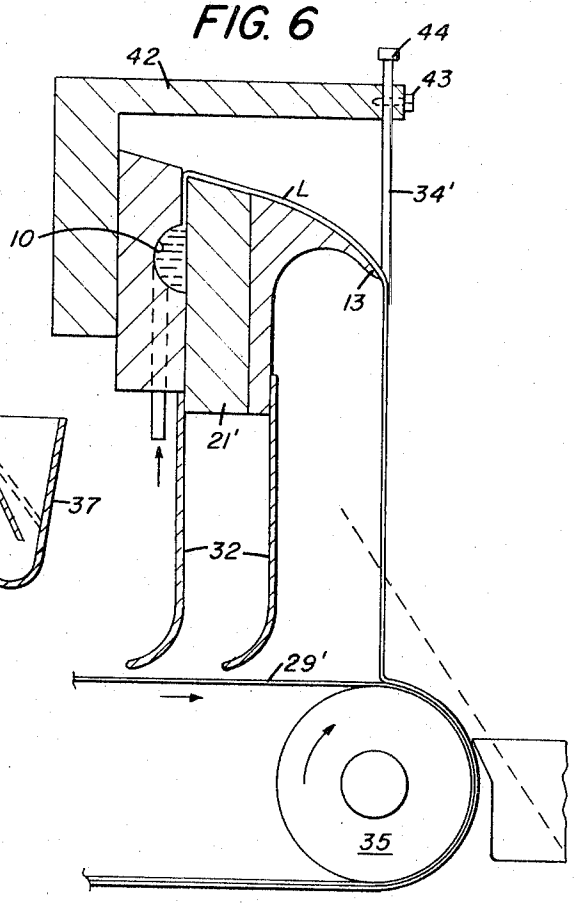


FIG. 7

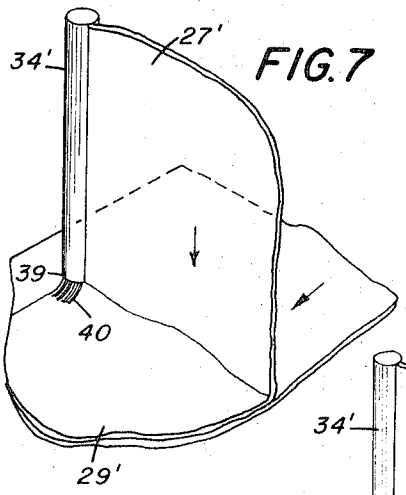


FIG. 8

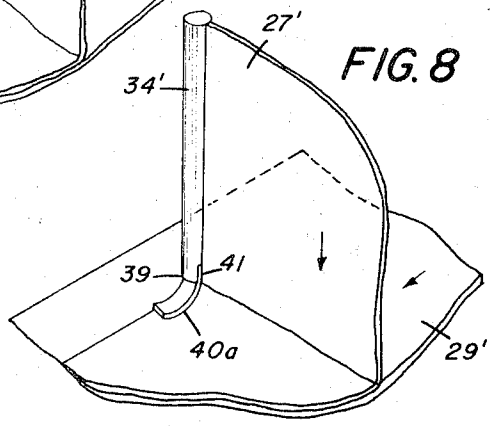


FIG. 5

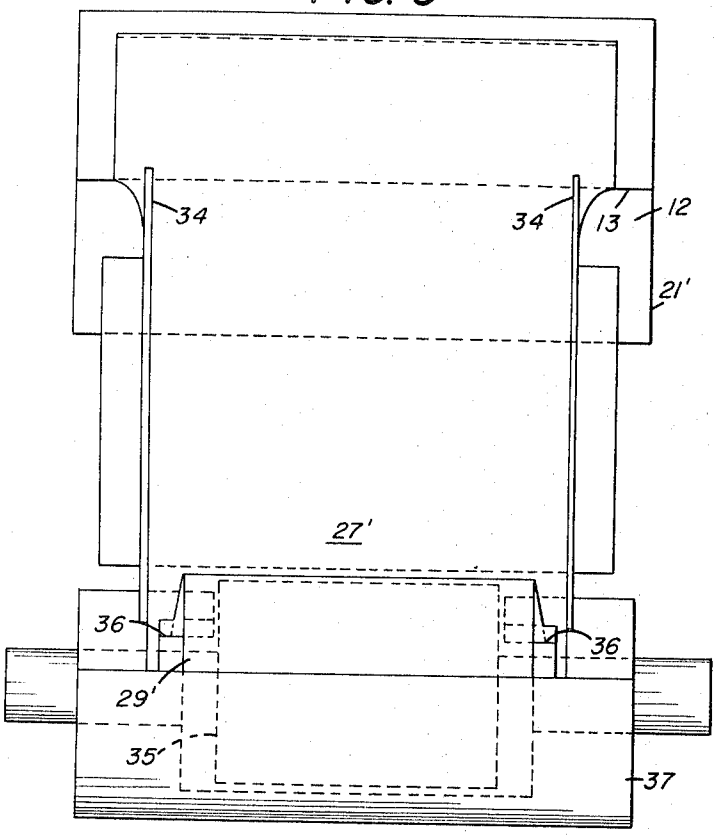


FIG. 9

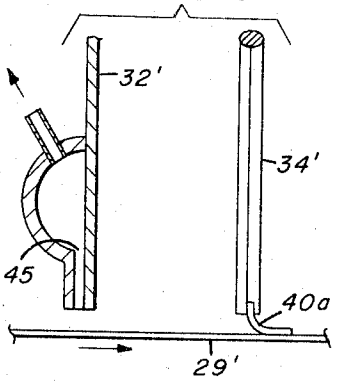


FIG. 11

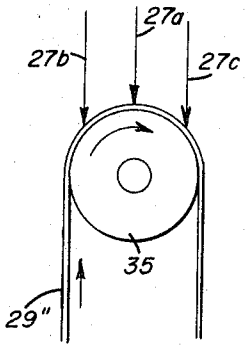


FIG. 10

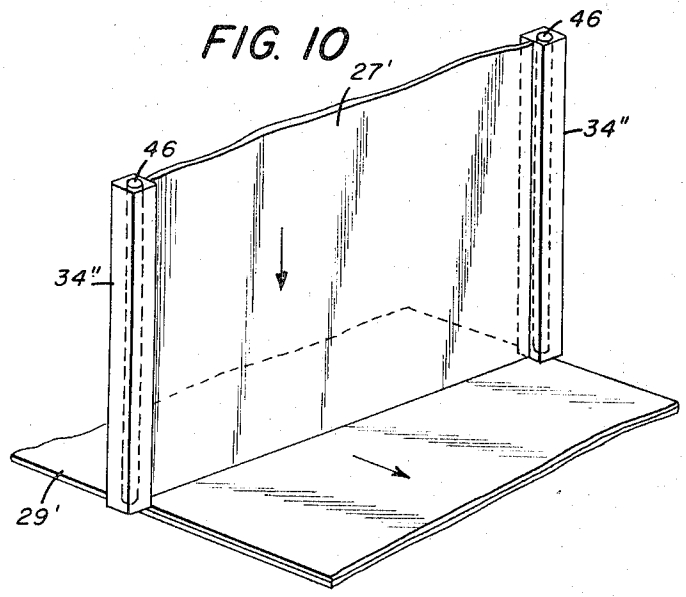


FIG. 12

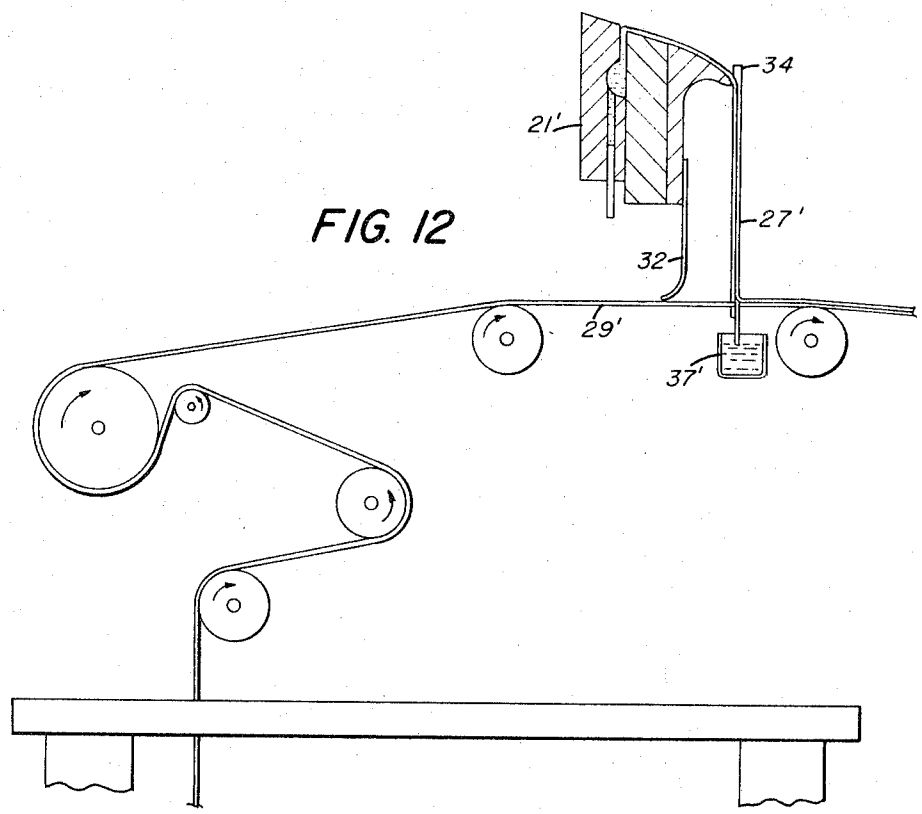

34
21'
27'
32
29'
37'

FIG. 13

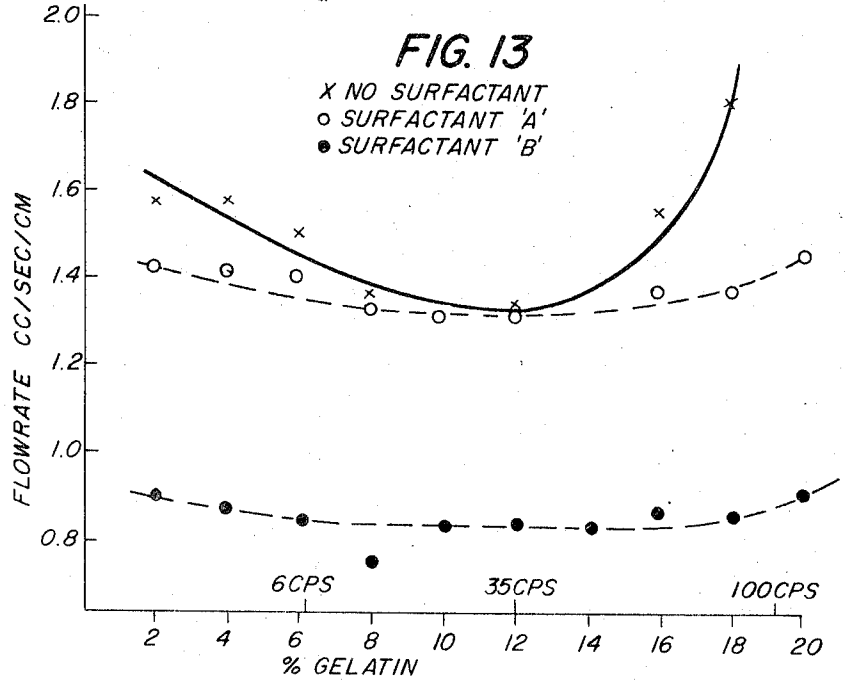

X NO SURFACTANT
o SURFACTANT 'A'
● SURFACTANT 'B'
FLOWRATE CC/SEC/CM
2.0
1.8
1.6
1.4
1.2
1.0
0.8
6CPS
35CPS
100CPS
2
4
6
8
10
12
14
16
18
20
% GELATIN

FIG. 14

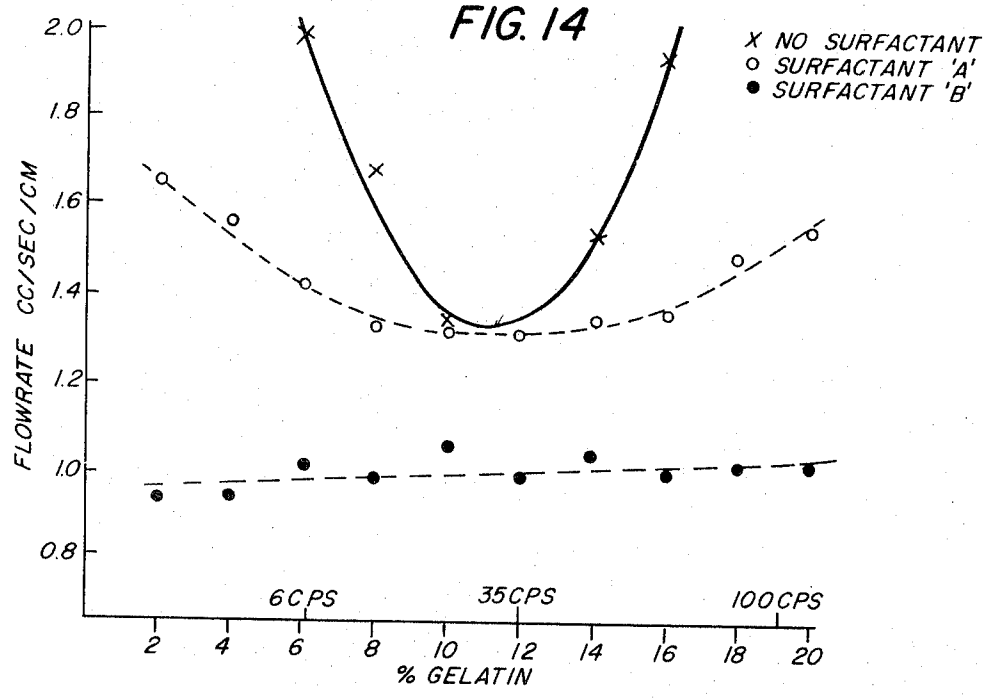

X NO SURFACTANT
○ SURFACTANT 'A'
● SURFACTANT 'B'
FLOWRATE CC/SEC/CM
2.0
1.8
1.6
1.4
1.2
1.0
0.8
6 CPS
35 CPS
100 CPS
2
4
6
8
10
12
14
16
18
20
% GELATIN

FIG. 15

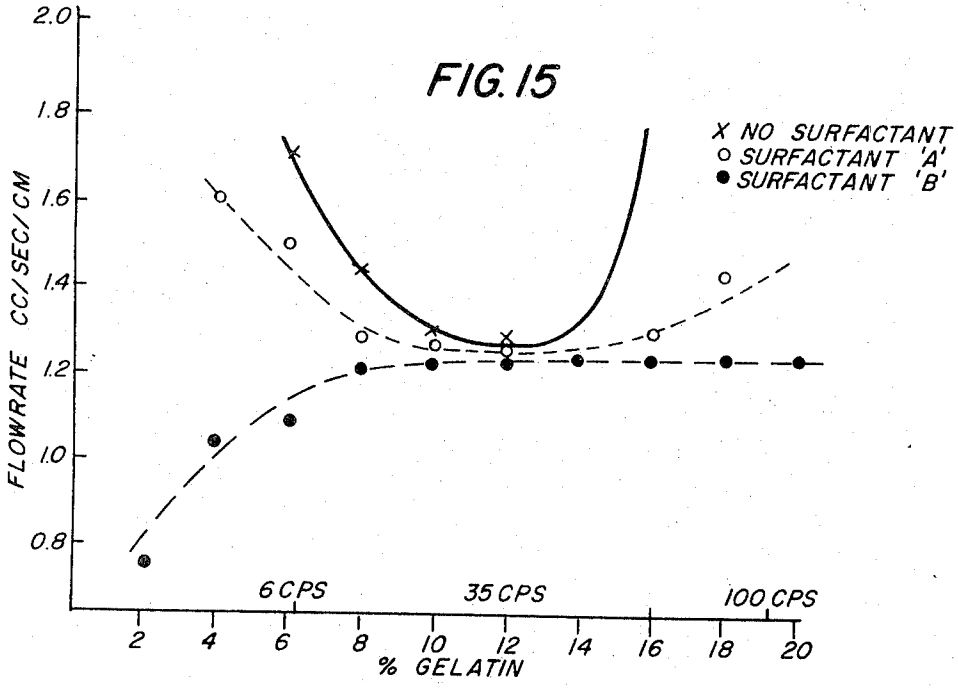
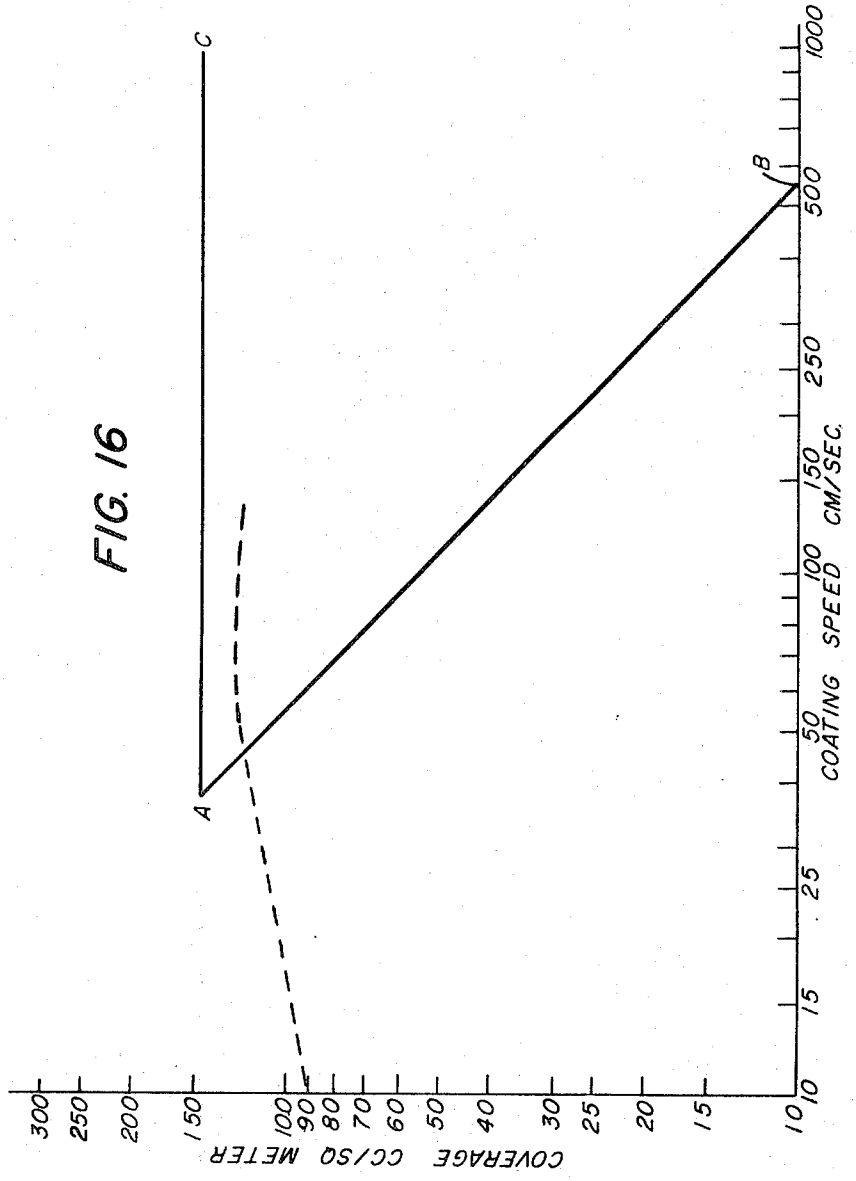

X NO SURFACTANT
○ SURFACTANT 'A'
● SURFACTANT 'B'
FLOWRATE CC/SEC/CM
2.0
1.8
1.6
1.4
1.2
1.0
0.8
6 CPS
35 CPS
100 CPS
2
4
6
8
10
12
14
16
18
20
% GELATIN

FIG. 16


C
B
A
1000
500
250
150
100
50
25
15
10
COATING SPEED CM/SEC.
300
250
200
150
100
90
80
70
60
50
40
30
25
20
15
10
COVERAGE CC/SQ METER

APPARATUS FOR PRODUCTION OF PHOTOGRAPHIC ELEMENTS

This application is a continuation of U.S. application Ser. No. 24,457, filed Mar. 16, 1970, now abandoned, which in turn is a division of U.S. application Ser. No. 733,944, filed June 3, 1968, now U.S. Pat. No. 3,632,374.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates in general to the manufacture of photographic elements comprising a support coated with at least one layer of a photographic coating composition and specifically to novel apparatus whereby the coating composition is applied to the support in the form of a thin uniform layer.

Photographic coating compositions typically consist of aqueous solutions or dispersions of hydrophillic colloids with or without other materials dissolved or dispersed therein. They are liquid compositions of relatively low viscosity, for example, a viscosity of less than about 150 centipoises, and most frequently in the range from about 5 to about 100 centipoises, and after being coated onto the surface of the support are subjected to controlled temperatures to effect setting and/or drying. Coating compositions are in use in the photographic art which differ greatly in chemical composition and also, to a more limited extent, in physical characteristics, and a number of different materials are in common use as the support. Thus, for example, the support may be made of paper, film base, glass, cloth and the like, and it may be coated in the form of discrete sheets or, as is more usually the case, in the form of a continuous web.

The manufacture of photographic elements is an extremely difficult art requiring extremely accurate control. Unlike coating operations in other arts, where complete coverage of the article being coated and attractive appearance are usually the only essentials, for any particular coating method to find application in the photographic art it must provide for precise and exacting control. In particular, a photographic element requires individual layers which are exceedingly thin, i.e., a wet thickness which is a maximum of about 0.015 centimeters and generally is far below this value and may be as low as about 0.001 centimeters. After coating, the layers have to be set and/or dried before the product can be handled and their surfaces generally cannot be subjected to any physical treatment to increase their smoothness and/or their thickness uniformity. For this reason, the coating composition must be applied to the support in such a precise manner that after the layer is set and/or dried it will be within permissible tolerances with respect to both thickness and uniformity. Since an individual layer must be extremely thin, as is indicated above, and since the maximum variation in thickness uniformity is plus or minus five per cent, and may in some instances be as little as plus or minus one per cent, it will be appreciated that the coating operation in the manufacture of photographic elements is an unusually complex and demanding procedure. Moreover, the difficulties involved in meeting the requirements of extreme thinness and extreme uniformity are further magnified by the fact that in order to be commercially practical the coating operation must be capable of handling continuous webs of as much as a meter or more in width and must permit the web to be coated at high speeds, for example, speeds

of as high as several hundred centimeters per second.

2. Description of the Prior Art

Although many methods of coating a support with a liquid coating composition to produce a photographic element have been developed over the years, present commercial practice is largely confined to the use of bead coating. In the bead coating technique, the surface of the web to be coated is moved across and in contact with a bead or puddle of the coating composition to pick up a layer of the composition therefrom. The coating composition is continuously fed to this bead or puddle at a rate at least as great as it is removed by the moving web. Maintenance and stability of the bead require that a supporting surface be spaced in close proximity, for example 0.02 to 0.04 centimeters, to the surface of the web. This supporting surface is generally a part of the coating apparatus which continuously feeds the coating composition from a supply source to the bead at the required rate. For example, as shown in U.S. Pat. No. 2,289,789, the supporting surface can take the form of a roller which dips into a reservoir of coating composition and carries the composition to the coating bead maintained between it and the surface of the web. On the other hand, as shown, for example, in U.S. Pat. No. 2,681,294, the necessary support can be provided by a hopper from which a stream of the coating composition is fed to a coating bead maintained between a lip of the hopper and the web, the rate of feed to the bead determining the wet thickness of the coating applied for any given web speed and coating composition viscosity.

The bead coating method, while a great advance in the art and of great value, has certain limitations which restrict its use. Thus, the width and uniformity of the gap between the surface of the web being coated and the hopper or roller feeding coating composition to the bead are quite critical. This gap must be very narrow, i.e., of the order of 0.02 to 0.04 centimeters and thus only slightly greater than the wet thickness of the layer of coating composition applied to the support. Such close spacing between the hopper, or roller, and the support to be coated has greatly complicated the manufacture of photographic elements. For example, this close spacing has resulted in excessive waste of product due to interruptions in the coating operation caused by a splice in the web passing the coating point. If the thickness of the splice is too great to permit it to pass the coating point, then the hopper or roller must be backed off to allow the splice to pass and then be returned to its operative position to reform the bead. On the other hand, even though the spacing is great enough to allow the splice to pass the coating point, its passage may disturb or disrupt the bead and alter the thickness and uniformity of the coating applied until the bead is properly re-established. In either case, re-establishment of the bead to give the desired coating takes some time and when high coating speeds are used a considerable length of product can be wasted during such periods. Furthermore, the close spacing which is necessary for stability of the bead allows minute particles or air bubbles which are present in the coating composition to be momentarily caught between the roller, or the lip of the hopper, and the support to form defects in the coating known in the photographic art as "pencil lines." Also, variations in the thickness of the support itself can be sufficient to alter the size and/or shape of the coating bead to such an extent as to intro-

duce irregularities in the thickness of the layer of coating composition applied to the support.

Other limitations on bead coating also restrict its usefulness. For example, bead coating is not adapted to the coating of individual or discrete sheets moved through the coating bead in succession by reason of the fact that the bead would be repeatedly broken and reformed as the sheets move therethrough. Furthermore, in bead coating the operable range of coverage, viscosity, and coating speed is not as broad as would be desirable. For example, to operate at high coating speeds it is ordinarily necessary to reduce the viscosity of the coating composition by diluting it with water or other liquid medium. However, the greater the extent of dilution the greater the amount of liquid which must be subsequently removed. Accordingly, the capacity of commercially practical drying equipment places practical limits on the extent to which the viscosity of the coating composition can be lowered by dilution while still permitting the coating to be dried, particularly when high coating speeds, as are now common in the photographic industry, are utilized. Thus, there are many instances where photographic coating compositions, because they are of higher viscosity than the viscosity most suitable for bead coating, cannot be handled by this method in an economical and convenient manner.

Photographic elements meeting the stringent specifications in force in the photographic industry are presently produced on a vast scale by the bead coating technique, but the serious disadvantages outlined above have hindered progress in improving product quality and reducing costs and in development of new products. It is toward the objective of providing apparatus for making photographic elements at least as good as those now made by bead coating, while effectively avoiding the disadvantages of bead coating hereinabove described, that this invention is directed.

SUMMARY OF THE INVENTION

The present invention provides novel apparatus for making a photographic element which comprises a support coated with at least one layer of a photographic coating composition. This invention is most closely connected with the prior art coating methods of bead coating and curtain coating; the former method, as hereinbefore described, being the most widely used method of making photographic elements and the latter method having been utilized heretofore in the painting and packaging arts to coat objects of many different types. However, in contrast with bead coating, in this invention the coating composition is applied to the support as a free-falling vertical curtain, and, unlike methods of curtain coating known heretofore, the apparatus disclosed herein provides exacting control of the means by which the free-falling curtain is generated and also upon maintaining certain critical relationships between the operating variables whereby, as was unexpectedly discovered by applicant, a free-falling curtain will provide the combination of extreme thinness and extreme uniformity which is essential in the coated layers of photographic elements. The use of a free-falling curtain to apply coating composition is new to the photographic art and the existing knowledge in the curtain coating art, as it has developed in the painting and packaging fields, would certainly deter one seeking a better way to make photographic elements from employing a free-falling curtain of coating composition. Thus, in view of the physical characteristics of photographic coating compositions, for example, the relatively low viscosity, further in view of the very low flow rates necessitated by the extreme thinness of the coated layers, and still further in view of the exacting specifications the product must meet, the operability of a method based on the use of a free-falling curtain in the photographic art is certainly an unexpected and surprising result. Moreover, the high quality of the product produced, when operation of the method is carefully controlled within the critical limits specified herein, represents a remarkable achievement to those skilled in coating methods utilized in the photographic art heretofore and familiar with the limitations and disadvantages associated therewith.

In accordance with this invention, a photographic element comprising a support coated with at least one layer of a photographic coating composition, is produced by apparatus adapted for moving the support to be coated along a path through a coating zone and forming from a liquid photographic coating composition a continuous, stable, free-falling, vertical curtain which extends transversely of the path and impinges on the face of the moving support to form thereon a uniformly thick layer of the coating composition. As described hereinafter in full detail, in carrying out this method the means whereby the curtain is generated must provide a uniform flow rate across the width of the curtain over substantially all of the region where curtain and support are coextensive, the magnitude of the flow rate must be sufficient to ensure stability of the curtain, and the flow rate and velocity at which the support is advanced must be coordinated in such manner as to ensure that a coating of precisely uniform thickness meeting the requirements of the photographic art is applied to the moving support. In a preferred embodiment, the apparatus of the invention also is adapted for causing the liquid coating composition to flow as a thin layer along a downwardly inclined slide surface, so that it will be accelerated by gravity at a rate less than acceleration in free fall, and then causing this layer to flow over the end of the slide surface as a free-falling curtain. This technique greatly facilitates establishment of the desired uniformity in flow rate across the width of the curtain with the added advantage, as hereinafter explained, of providing low initial momentum in the free-falling curtain. Advantageously, the thin flowing layer is produced by feeding the coating composition through a horizontally disposed, elongated, narrow slot from which it flows along the downwardly inclined slide surface.

In a preferred embodiment, apparatus according to this invention comprises means for moving the support to be coated along a predetermined path at a preselected speed through a coating zone; a hopper for the coating composition which has an elongated uniform discharge opening from which the coating composition is discharged; and a continuous supporting surface for the coating composition including a downwardly inclined slide surface preceding and terminating in a lip spaced vertically above the coating zone, the coating composition flowing by gravity down the slide surface to establish a thin and uniform layer by the time it flows over the lip to thereby form a free-falling curtain. Advantageously, means are also provided for varying the vertical spacing between the hopper lip and the moving support, and thereby regulating the height of the free-

falling curtain, for varying the speed at which the support is moved, and for varying the rate at which the coating composition is supplied to the hopper.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a vertical section of one form of coating hopper which can be used in making photographic elements according to the method of this invention.

FIG. 2 is a partial vertical section of a preferred type of coating hopper which is especially well adapted to the application of photographic coating compositions in accordance with this invention.

FIG. 3 is a perspective view of a modified form of the hopper of FIG. 1 shown in association with a moving web.

FIGS. 4 and 5 are, respectively, vertical cross-sectional and front elevational views of a preferred embodiment of coating apparatus in accordance with the present invention.

FIG. 6 is a vertical cross sectional view of a modified form of the coating apparatus shown in FIG. 4.

FIGS. 7 and 8 are perspective views of preferred alternative forms of edge guides for the free-falling vertical curtain.

FIG. 9 is a diagrammatic side elevation of a modified form of air shield incorporating a vacuum extractor for removing entrained air from the surface of the support to be coated.

FIG. 10 is a diagrammatic perspective view of a modified form of edge guide for stabilizing the free-falling vertical curtain.

FIG. 11 is a schematic view illustrating how the position of the free-falling vertical curtain can be adjusted relative to the axis of a roller supporting a web to be coated.

FIG. 12 is a schematic view of another arrangement of coating apparatus which can be used in practicing the present invention.

FIGS. 13 to 16 are graphical representations of results obtained in coating aqueous gelatin solutions in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As hereinbefore described, this invention involves application of the liquid photographic coating composition to the support by generating a free-falling vertical curtain of the coating composition and causing this curtain to impinge on the moving support. By virtue of the forces acting on such a curtain, it will decrease in thickness as it falls, i.e., the velocity of the falling liquid will increase as a result of gravitational force so that the thickness of the curtain must decrease proportionately. However, applicant has discovered that if the free-falling curtain is initially generated so that it is free of any turbulence or non-uniformity, i.e., so that the flow rate is the same at all points along a line traversing the curtain widthwise, then the curtain will retain this characteristic as it falls, even to a point where it has become extremely thin, and the layer of coating composition applied to a support advanced through this free-falling curtain will be uniformly thick. It has also been discovered that in order to obtain a uniform flow rate across the width of the curtain, within the exacting limitations essential in the manufacture of photographic elements, the means employed to generate the curtain should function in such manner that the initial momentum of the falling liquid, i.e., the momentum at the start of free fall, will be low. In other words, in practicing this invention the downward velocity of the liquid as it leaves the means whereby the free-falling curtain is formed and enters the curtain itself should be as small as can be attained in a practical manner. More specifically, it is preferred that this downward velocity be less than about 20 centimeters per second and particularly preferred that it be less than about 10 centimeters per second.

The velocity of the falling liquid at the bottom end of the free-falling curtain utilized in the method of this invention, i.e., the impingement velocity, will be the sum of the initial downward velocity imparted to the liquid and the velocity acquired during free fall as a result of the force of gravity. This impingement velocity can be made quite high as a result of extending the height of free fall to a considerable distance and yet the curtain will retain the uniformity which is essential to the practice of this invention as long as it is generated in such manner that the flow rate is uniform at all points along a line traversing the curtain widthwise and is protected from any disturbing influences, such as air currents, during free fall.

Since the free-falling curtain can be greater in width than the support being coated, as hereinafter described, it will be apparent that uniformity in flow rate is necessary only in the region where the curtain and the support are coextensive. Moreover, since a portion of the coated support extending along each longitudinal edge can be trimmed off and discarded to avoid problems arising from non-uniformity in layer thickness adjacent the edges, it is not essential that there be uniformity in flow rate to the outer limits of this region. Accordingly, operation of the method of this invention is practical as long as the curtain has a uniform flow rate over at least a major part of its width and over substantially all of such portion of its width as is coextensive with the support.

Stability of the free-falling vertical curtain, i.e., continuous flow without a break occurring anywhere in the curtain, is achieved, in accordance with this invention, by providing a flow rate of liquid photographic coating composition of at least about 0.5 cubic centimeters per second per centimeter of curtain width. Thus, the free-falling curtain must be generated so as to have at least this minimum flow rate while also satisfying the requirement of uniformity in flow rate across its width, as discussed above. Moreover, although these two criteria are necessary, they are not alone sufficient for successful production of photographic elements. In this regard, it has been discovered that in order to achieve the combination of extreme thinness and extreme uniformity essential in the coated layers of photographic elements it is also necessary that the ratio of the flow rate, measured in cubic centimeters per second per centimeter of curtain width, to the velocity at which the support being coated is advanced, measured in centimeters per second, be less than about 0.015.

In summary, the critical limits defining the method of this invention, which render the use of a free-falling curtain applicable to the production of photographic elements contrary to what would be expected in light of prior knowledge in the curtain coating art, are the formation of a free-falling curtain with a flow rate of at least about 0.5 cubic centimeters per second per centi-

meter of curtain width and also with uniformity in flow rate as hereinabove described, and a correlation between flow rate and the speed at which the support is advanced such that the ratio of the flow rate to the velocity of the support is less than about 0.015.

It should be especially noted that in practicing the method of this invention it is advantageous to utilize techniques in forming the free-falling curtain which differ from those commonly used in curtain coating methods employed in the painting and packaging arts. Thus, for example, it is common practice in the prior art to produce a free-falling curtain by allowing the liquid to flow over a weir, but this method will inevitably caused variations in thickness and/or turbulence in the curtain and is not capable of producing the degree of uniformity necessary for use in making photographic layers. Even though this technique provides for low initial momentum in the falling liquid, a result described hereinabove as desirable, it is not suitable for use in the method of this invention because it does not also provide the essential uniformity. On the other hand, the common practice in the curtain coating art wherein the liquid is extruded under high pressure from a discharge slot is also unsatisfactory in the method of this invention. Thus, when low viscosity liquids, such as photographic coating compositions, are fed from an extrusion-type hopper under high pressure the emerging liquid has an incipient turbulence with the result that "lines" develop in the falling curtain (known as "slot flow lines"). These lines will also be present in the dried coating and thus render the coated layer unacceptable for photographic use. Moreover, it has been discovered that a more stable free-falling curtain is formed at low flow rates, such as the rates which must be employed in making photographic elements, if the velocity at which the coating liquid enters the free-falling curtain is at a minimum, rather than at a relatively high velocity as would be true if the liquid were discharged under high pressure from the discharge slot in accordance with conventional practice in the curtain coating art.

It should also be appreciated that since precise coating thickness is not necessary in those fields in which curtain coating techniques have been heretofore employed, the flow rate can be altered at will whenever curtain instability problems arise so as to re-establish stable conditions. However, it will be apparent that this could not be done in the manufacture of photographic elements where the thickness of the coated layer must be maintained within exacting standards. Moreover, in the practice of curtain coating in the prior art, as utilized, for example, in application of paint or lacquer to furniture, if an article is imperfectly coated it is simply returned to the coating line to receive a second coat which will cover up any imperfections in the first coat. Such procedure is obviously not applicable to production of photographic elements where the coating composition must ordinarily be applied to a continuous web of great length and where recoating would result in excessively thick and/or non-uniform coated layers.

With regard to the prior art methods of curtain coating referred to above, a number of patents and technical publications are available. Reference may be made, for example, to U.S. Pat. Nos. 3,067,060, 3,132,968, 3,205,089 and 3,341,354. Theoretical aspects of curtain coating are discussed in, for example, Journal of Fluid Mechanics, Vol. 10, Part 2, pages 297–305 (1960) and *Modern Plastics*, 40, 134 (1962).

Referring now to FIG. **1**, there is shown apparatus for applying a liquid photographic coating composition to the surface of a support in accordance with the present invention. The apparatus comprises a hopper **21** supplied with a liquid photographic coating composition via entrance **22** and having an elongated discharge slot **23** in the bottom thereof whose width may be varied by means of eccentric **22'**. The hopper **21** and the discharge slot **23** extend transversely of the path of travel of a support, i.e., a web or individual sheet, to be coated, the path of travel of the support being indicated at P. End plates **24** at each end of hopper **21** adjustably support the hopper and also act as edge guides for the free-falling vertical curtain **27** of coating liquid issuing therefrom. Located beneath the hopper and below the coating path P is a catch tray **25** for catching surplus coating liquid, which may be recirculated to the hopper **21** by suitable means (not shown) after passing through suitable means for removing air bubbles therefrom (not shown), as are known in the photographic art. Located within the catch tray **25** is an anchor bar **26** which assists in the initial establishment of the free-falling vertical curtain **27** and reduces the formation of air bubbles in the excess coating flowing into the catch tray by minimizing the tendency for the coating liquid to splash as it enters the tray.

In operation, a liquid photographic coating composition, e.g., silver halide/gelatin emulsion, is supplied to the hopper at a rate of at least about 0.5 cubic centimeter per second per centimeter of curtain width to maintain a stable free-falling curtain **27** of liquid between the end plates **24.** It is noted that instead of the coating liquid being extruded under pressure through the discharge slot **23** to form the curtain, as is common in the curtain coating art, the top of the hopper is open to the atmosphere and the coating liquid is merely fed into the hopper to maintain a supply having a fixed head from which the curtain is formed by gravity flow through the discharge slot. This particular method of forming the free-falling curtain provides the desired low initial momentum in the falling liquid. In some instances, it may be necessary to taper discharge slot **23** toward the entrance **22** to compensate for any variation in head along the length of the slot resulting from the fact that the hopper is fed at only one end and thereby ensure a uniform flow rate. It has been found that by using this type of hopper with a gravity feed the layer of liquid formed by passing through the discharge slot will enter the curtain **27** at a low velocity, e.g., less than 10 centimeters per second, and that as a result of this a very stable curtain can be formed with low viscosity solutions at low flow rates, as required in making coatings in the manufacture of photographic elements. To permit an adjustment of the height of the free-falling vertical curtain **27,** for reasons which will be discussed more fully below, the hopper **21** is mounted on the end plates **24** so that it can be adjusted vertically relative to the coating path P. To this end, adjusting means comprising a rack R on the hopper engaged by a pinion R' may be provided.

FIG. **2** shows another form of hopper **21'** for forming the free-falling curtain. This hopper is preferred because by its use it is possible to more readily obtain a stable free-falling curtain using low rates of low viscosity liquid than with the extrusion-type hopper shown in

FIG. 1. Here, a liquid photographic coating composition if fed, at a constant rate commensurate with the thickness of the coating desired on a support moved through the coating zone at a given speed, by a constant feed pump, not shown, into a relatively large cavity 10 and thence vertically upward through a narrow, elongated discharge slot 11 and out onto a downwardly inclined slide surface 12. The layer L of liquid issuing from the discharge slot 11 is substantially uniformly thick and flows down the slide surface 12 under the force of gravity. By the time it reaches and flows over the lower edge or lip 13 of the slide surface to form the free-falling vertical curtain 27' it has become almost exactly uniform in thickness. In addition to this type of hopper, generally referred to as a slide hopper, forming a moving layer of liquid of very uniform thickness prior to formation of the free-falling curtain, the velocity of such layer at the time it enters the curtain is close to zero in a vertically downward direction and hence the momentum of the curtain at its point of origin is at a minimum. As a result, vertical free-falling curtains of photographic coating liquids formed in this manner have been found to possess very good thickness uniformity and to be surprisingly stable despite the low rate and the low viscosity of the coating liquid. This is particularly true if a surfactant is added to the coating liquid, as discussed hereinbelow, since the slide surface apparently allows time for the surfactant to diffuse to the air interface to the flowing layer of liquid before it forms the curtain, and thus lowers the surface tension of the free-falling vertical curtain to further increase its stability. The support to be coated is not shown in FIG. 2. However, it is moved at a constant speed through the coating zone, as explained elsewhere herein.

FIG. 3 is a perspective view of a slightly modified coating apparatus of the type shown in FIG. 1 and illustrates more clearly the manner in which a support is passed through the free-falling curtain to have its surface coated. It will be seen that the longitudinal edges of the free-falling curtain 27'' emanating from the hopper 21'' engage vertical edge guides 24' which extend beyond and below the opposite edges of the support 29 to be coated, in this case a continuously moving web, and into a catch tray, not shown. The edge guides 24'' serve to help form the vertical curtain 27'' and also to restrain the edges of the curtain from "necking in" (a phrase used to refer to narrowing of the edge to edge curtain width) during the free fall so as to maintain uniformity across a width sufficient to cover the entire width of the support to be coated. In this connection, the edge guides 24' serve in the same capacity as the end plates 24 of the apparatus shown in FIG. 1. Since the curtain tends to be thicker adjacent to the edge guides, if those guides were placed at or within the edges of the support to be coated, then the coating applied at the edges of the support would be thicker than that applied to the major portion of the support. This would complicate the drying problem unless the edges of the support were subsequently trimmed off. In order to overcome these problems, the curtain 27'' is generally made wider than the support to be coated to ensure that the coating applied to the support is of uniform thickness right to its edges. The overflow of coating at the edges of the support is caught in a catch tray and recirculated to the hopper.

FIGS. 4 and 5 illustrate a preferred embodiment of coating apparatus for applying a layer of photographic coating composition onto the surface of a continuous support. As shown, the apparatus includes a slide hopper 21' essentially like that shown in FIG. 2. As before, a liquid photographic coating composition is fed at a uniform rate by a constant feed pump, not shown, into a cavity 10 and thence vertically upward through a narrow, elongated discharge slot 11 and out onto a downwardly inclined slide surface 12. The layer of liquid L issuing from the discharge slot 11 is substantially uniformly thick, is wider than the support to be coated, and flows down the slide surface 12 under the force of gravity. At the time it flows over the lip 13 of the slide surface this layer has become of almost exactly uniform thickness so that the free-falling vertical curtain of coating liquid 27' is established with initial uniform thickness. In this instance, the slide surface is arranged at an angle of approximately 15° to the horizontal. So that the layer of liquid flowing down this slide surface will flow cleanly off the end thereof, the surface terminates in a lip having a radius of about 2.5 centimeters, or less, and is undercut at its lower surface to an angle approximately 30° above the horizontal. The vertical free-falling curtain of liquid 27' impinges upon a continuous web 29' as it passes over and around a supporting roll 35 which in turn forms a part of means for moving the web at a substantially constant speed through the coating zone. As shown in FIG. 5, the width of the free-falling curtain 27' is somewhat greater than the width of the support 29' to be coated, and to prevent the overflow of liquid at the edges of the support from running down the ends of the roll 35 the roll is made narrower than the web. For reasons hereinafter discussed, it is desirable that it be possible to adjust the height of the free-falling curtain 27' in order to achieve an optimum height for a given set of conditions. To this end, the hopper 21' can be adjustably mounted on vertical supporting end plates (see FIG. 1) so that the vertical spacing of the lip 13 above the coating point on roll 35 can be readily increased or decreased as desired.

As shown most clearly in FIG. 5., two spaced, small diameter, rod-like edge guides 34 extend vertically downward from the lip 13 to engage and constrain the longitudinal edges of the free-falling curtain 27'. The lower ends of the edge guides are spaced beyond the edges of the web 29' and extend into individual catch trays 36 which in turn conduct the excess coating which overflows the edges of the web to a main catch tray 37 located forwardly of the roll 35, and from which tray the excess liquid can be recirculated to the hopper by means not shown. Looking at FIG. 5, it will be observed that the edge guides 34 are shown spaced so that the edges of the layer L of liquid moving down the slide surface "neck in" slightly to engage the edge guides, but this arrangement is not essential and, if desired, the edge guides may be spaced apart a distance equal to the width of the layer as it leaves the slide surface.

As shown in FIG. 4, fixed to and depending downwardly from the hopper 21' are one or more curved air shields 32 which extend to a region closely adjacent the plane of the web 29' being coated. It will be appreciated that as the height of the hopper above the coating point is adjusted the length or position of the air shields should be changed accordingly to maintain them closely adjacent the moving web. These air shields are provided to protect the free-falling curtain from air currents and to remove entrained air from the surface

of the support just before it reaches the coating zone. The shields reduce the thickness or stability of the air barrier on the support surface which the falling curtain must penetrate to ensure an even application of the coating composition on the support. A curtain deflector **38**, shown only in FIG. **4**, is positioned between the edge guides **34** with its lower end extending into the catch tray **37**. This deflector **38** is pivotally mounted to move between the position shown in broken lines in FIG. **4**, wherein it intercepts the free-falling curtain **27'** and directs it into tray **37**, to an inoperative position shown in full lines, wherein it allows the curtain **27'** to impinge upon web **29'**. In an alternate embodiment, deflector **38** can be slideably mounted rather than pivotally mounted and is then preferably positioned so as to intersect free-falling curtain **27'** just above web **29'**.

In operation, a coating liquid is pumped by a constant feed gear pump, or the like, not shown, into the cavity **10** at a rate commensurate with the thickness of the layer of liquid desired to be coated onto the surface of the web **29'**. The coating liquid exits through the elongated, narrow discharge slot **11** to form on the slide surface **12** a layer L of liquid which is substantially of uniform thickness adjacent to the slot. This layer of liquid then flows down the slide surface under the force of gravity and by the time it reaches the lip **13** it is of almost exactly uniform thickness. This layer then passes over the lip at a low velocity and forms the free-falling curtain **27'** which is also uniform in thickness adjacent to the lip, has an initial momentum which is practically zero, and has a low and uniform flow rate at all points along any line across its width. The free-falling curtain **27'** is deflected into the catch tray **37** by deflector **38** until a stable curtain is established and the web to be coated is accelerated up to the required speed. The deflector **38** is then pivoted from the path of the falling curtain allowing it to fall onto and coat the web with a thin uniform layer of liquid.

Should it be found undesirable for any reason to recirculate the excess coating liquid flowing beyond the edges of the support, the modified forms of edge guides shown in FIGS. **7** and **8** may be used. Referring first to FIG. **7**, the lower end or foot **39** of each edge guide **34'** has attached thereto a trailing brush **40** composed of a few hairs, the foot **39** being spaced approximately 0.3 cm to 0.6 cm above the surface of the web **29'** to be coated and the bristles of the brush extending 1.25 cm below the foot so that they ride on the surface of the web. By this arrangement, the curtain **27'** can, if desired, be of the same width as the support to be coated. This not only eliminated any problem which might arise where an overflow of coating liquid at the edges of the support is required, as in the embodiment illustrated in FIGS. **4** and **5**, but it also permits the roll **35** to be of equal or greater length than the width of the support to be coated, thereby allowing one length of roll to be used for all web widths to be coated. Also, an uncoated section or sections can be provided transversely of the web by using additional edge guides to divide the curtain **27'** into two or more curtains, each of lesser width than the web.

FIG. **8** illustrates a preferred embodiment of the arrangement shown in FIG. **7**. In this embodiment, each edge guide **34'** (again in the form of a small diameter rod of, for example, stainless steel) has an axial slot **41** in its foot **39** into which is fitted a strip **40***a* of a flexible, resilient material. This strip **40***a* is advantageously a strip of photographic film base, but may also be a strip of stainless steel of the required resilience and flexibility. The edge guides are oriented so that the strips **40***a* riding on the surface to be coated trail and are splayed laterally toward the edges of the web **29'**. Such an arrangement tends to spread out the excess coating liquid which occurs at the edges of the sheet **27'** by reason of the coating liquid surrounding and running down the edge guides. As mentioned above, the edge guides **34'** may be so spaced that the strips **40***a* cause the curtain **27'** to coat right up to the edges of the web **29'**, or as shown in FIGS. **7** and **8**, they can be adjusted so that the curtain coats to any selected point inside of the edge of the support. The spreading action afforded by these improved forms of edge guides is primarily beneficial in that it equalizes the drying load at all points across the coated web and permits the entire coated web to be dried at the same time.

If the edge guides **34'** of the form shown in FIGS. **7** and **8** are used, it is desirable that they be rotatably adjustable. To this end, as shown in FIG. **6**, the hopper **21'** is provided with a cap **42** extending over the top thereof. The cap **42** supports a clamping bar **43** at its end in alignment with the leading edge of the lip **13**. The clamping bar serves to retain the edge guides **34'** in a selected position transversely of the hopper **21'** and in a vertical position relative to the roll **35**. Each edge guide is of the form described in relation to FIG. **8** and is provided with a knob **44** whereby the guide can be rotated so as to vary the angular trailing relation of the strip **40***a* relative to the path of the support. It will be seen that in this embodiment no catch trays are provided since the free-falling curtain is never wider than the web to be coated. Air shields **32** fixedly secured to hopper **21'** extend closely adjacent to web **29'** to reduce the air barrier, as previously described.

FIG. **9** illustrates a further modification which is useful in coating apparatus according to the present invention. In the arrangement shown the air shield **32'** is straight instead of curved and is provided with a vacuum manifold **45** which is positioned adjacent the web to be coated and connected to a vacuum pump (not shown) to withdraw air therefrom as indicated by the arrow. By this arrangement, not only is the free-falling curtain shielded from ambient air currents to enhance its stability, but some of the air entrained by web **29'** is drawn off the surface just before it reaches the free-falling curtain. Here the ends of the edge guides **34'** are shown as being provided with a trailing strip **40***a* as illustrated in FIG. **8**.

FIG. **10** illustrates another modification which is applicable to any of the edge guides mentioned above and which assists in maintaining a stable curtain even at very low flow rates. In this arrangement, each of the edge guides **34''** is hollow and is provided with an axial slot along that side thereof to which the curtain adheres. A porous tube **46** extends axially of each of the hollow edge guides and an inert liquid, for example a clear gelatin solution, is pumped into the top of the tube so as to exude from the axial slots in the edge guides **34''**.

Although it is preferred to coat the web while it is rigidly supported, as by a roll **35** as disclosed previously, this is not essential as coatings have also been made with apparatus such as that illustrated in FIG. **12**. The arrangement there illustrated shows a slide hopper **21'** forming a vertical free-falling curtain **27'** between edge

guides 34 spaced wider apart than the width of the web 29′ to be coated, a catch tray 37′ being positioned therebeneath for collection and recirculation of coating liquid. In this apparatus, that portion of the web 29′ passing through the free-falling curtain 27′ is placed under tension to keep it from vibrating excessively as it passes the coating point. Any of the edge guides previously described, as well as the different types of previously described air shields and hoppers, can be used with the arrangement shown here. As mentioned before, the web feeding means of this apparatus can be adjustable so that the speed at which the web is moved through the free-falling curtain can be varied to meet different coating requirements, as desired.

FIG. 11 is a schematic view which illustrates that it is not necessary that the free-falling curtain be oriented to intersect the axis of the supporting roll 35 in order to satisfactorily coat a web passing therearound. As shown in FIG. 11, if the web 29″ to be coated is directed to and from the supporting roll 35 so as to leave sufficient supported area of the web accessible then the free-falling curtain can be directed on axis with the roll, as indicated by arrow 27*a*, or off axis of the roll as shown by arrows 27*b* and 27*c*, and a satisfactory coating will be applied to the web. It will be appreciated that the free-falling curtain should not be so far off axis that the direction of travel of the web at impingement is so far from horizontal as to detrimentally affect the coating operation.

The method of this invention is suitable for use with any liquid photographic coating composition and can be employed with any type of photographic support and it is, accordingly, intended to include all such coating compositions and supports as are utilized in the photographic art within the scope of these terms, as employed herein and in the appended claims.

The term "photographic" normally refers to a radiation sensitive material, but not all of the layers presently applied to a support in the manufacture of photographic elements are, in themselves, radiation sensitive. For example, subbing layers, pelloid protective layers, filter layers, antihalation layers, etc., are often applied separately and/or in combination and these particular layers are not radiation sensitive. The present invention relates also to the application of such layers, and the term "photographic coating composition," as employed herein, is intended to include the compositions from which such layers are formed. Moreover, the invention includes within its scope all radiation sensitive materials, including electrophotographic materials and materials sensitive to invisible radiation as well as those sensitive to visible radiation. While, as mentioned hereinbefore, the layers are generally coated from aqueous media, the invention is not so limited since other liquid vehicles are known in the manufacture of photographic elements and the invention relates also to the use of such liquid vehicles.

More specifically, the photographic layers coated according to the method of this invention can contain light-sensitive materials such as silver halides, zinc oxide, titanium dioxide, diazonium salts, light-sensitive dyes, etc. as well as other ingredients known to the art for use in photographic layers, for example, matting agents such as silica or polymeric particles, developing agents, mordants, and materials such as are disclosed in U.S. Pat. No. 3,297,446. The photographic layers can also contain various hydrophillic colloids. Illustrative of these colloids are proteins, e.g., gelatin; protein derivatives; cellulose derivatives; polysaccharides such as starch; sugars, e.g., dextran; plant gums; etc.; synthetic polymers such as polyvinyl alcohol, polyacrylamide, and polyvinylpyrrolidone; and other suitable hydrophillic colloids such as are disclosed in U.S. Pat. No. 3,297,446. Mixtures of the aforesaid colloids may be used, if desired.

In the practice of this invention, various types of photographic supports may be used to prepare the photographic elements. Suitable supports include film base, e.g., cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polycarbonate film, polystyrene film, polyethylene terephthalate film and other polyester films; paper; glass; cloth; and the like. Paper supports coated with alpha-olefin polymers, as exemplified by polyethylene and polypropylene, or with other polymers, such as cellulose organic acid esters and linear polyesters, may also be used if desired. The support can be in the form of a continuous web or in the form of discrete sheets, but in commercial practice it will most frequently take the form of a continuous web.

Optimum conditions for carrying out the method of this invention will depend, in part, upon the physical properties of the particular liquid photographic coating composition and support involved. Thus, for example, the characteristics of the free-falling vertical curtain, and in particular its stability, are influenced by such physical properties as the viscosity and surface tension of the coating composition, and the uniformity of the coating applied to the support is influenced by such factors as the smoothness and wetting characteristics of the support.

Photographic coating compositions are liquids of relatively low viscosity, i.e., viscosities from as low as about 2 centipoises to as high as about 150 centipoises, or somewhat higher, and most commonly in the range from about 5 to about 100 centipoises. However, as previously explained, it has been discovered that adequate stability of the free-falling vertical curtain is attainable in spite of this low viscosity and that the desired uniformity and extreme thinness in the coated layer can be achieved by operating within the limits hereinbefore described. The surface tension of photographic coating compositions also varies depending on the nature of the composition. Surface tensions of, for example, aqueous gelatin solutions are typically in the range of from 40 to 50 dynes per centimeter. In view of this rather high surface tension, it is generally advantageous in the practice of this invention to incorporate surfactants in the photographic coating composition in order to reduce the surface tension and thereby increase the stability of the free-falling vertical curtain.

Various types of surfactants can be used to modify the surface tension and coatability of photographic coating compositions in accordance with this invention. Useful surfactants include saponin; non-ionic surfactants such as polyalkylene oxides, e.g., polyethylene oxides, and the water-soluble adducts of glycidol and alkyl phenol; anionic surfactants such as alkylaryl polyether sulfates and sulfonates; and amphoteric surfactants such as arylalkyl taurines, N-alkyl and N-acyl beta-amino propionates; alkyl ammonium sulfonic acid betaines, etc. Illustrative examples of useful surfactants of these types are disclosed in British Pat. No. 1,022,878 and in U.S. Pats. Nos. 2,739,891, 3,026,202 and 3,133,816.

To enhance the uniformity of the coated layer applied to the surface of the support in accordance with this invention it is, in some instances, also desirable to modify the surface characteristics of the support. Thus, certain supports have surfaces which are not readily wet by certain coating compositions and where this is the case the uniformity of the coated layer can be significantly improved if the surface of the support is prewet before it reaches the coating zone. This prewetting operation does not necessarily require the application of a liquid to the surface, as the term might imply, but may include steaming the surface, passing it through a vacuum chamber in the presence of steam, etc. This prewetting tends to reduce the air barrier on the surface of the support as well as to reduce any natural repellency the surface may have for a given coating composition.

It should be noted that the method of this invention permits selection of coating speed, i.e., the speed at which the support is advanced through the coating zone, within a very broad range. The minimum speed which can be employed in a given instance is dependent upon the flow rate of the coating composition and is determined in accordance with the criterion hereinbefore disclosed that the ratio of the flow rate to the velocity of the support must be less than about 0.015. However, as long as this minimum is exceeded then the support may be advanced at any speed that is practical.

The wet thickness of the layer of coating composition deposited on the moving support will be the same as the thickness of the free-falling curtain just before impingement where the velocity of the support is equal to the impingement velocity. On the other hand, where the velocity of the support is greater than the impingement velocity then the wet thickness of the layer deposited will be less than the thickness of the curtain just before impingement, with greater and greater support velocities resulting in correspondingly thinner and thinner coatings. High support velocities are permissible since the free-falling curtain will remain vertical, rather than being pulled out in the direction the support is traveling, as long as the momentum of the curtain at impingement is sufficient to break the air barrier present on the surface of the moving support and the coating composition readily wets the support surface. Accordingly, there is no apparent upper limit on the velocity at which the support can be advanced except as dictated by practical considerations. Operation at speeds of several hundred centimeters per second and up to as high as about 1,500 centimeters per second or even higher is entirely feasible. Where the velocity at which the support is moved is less than the impingement velocity of the free-falling curtain the wet thickness of the layer of coating composition deposited on the support will be greater than the thickness of the curtain just before impingement. If this difference in velocity is not too great a uniformly thick layer can still be attained, until finally a point is reached where the free-falling curtain will fold back upon itself and thereby result in nonuniformity in coating thickness which would render the photographic element useless. The point at which the free-falling curtain will fold back upon itself is reached much sooner with coating compositions of low viscosity, e.g., 5 centipoises, than with coating compositions of higher viscosity, e.g., 100 centipoises. In accordance with this invention, satisfactory results with photographic coating compositions are ensured by operating within the limit on ratio of flow rate to support velocity hereinbefore disclosed.

To increase the support velocity at which good coating results can be obtained, means are preferably provided, in accordance with this invention, to reduce the thickness of the boundary layer of air at the surface of the support immediately before the support passes through the free-falling vertical curtain. This air barrier varies with the surface characteristics of the support, generally being greater for rough surfaces than for smooth ones, as evidenced by the fact that photographic film base presents a lesser air barrier to the coating liquid than photographic paper. Also, the air barrier is found to be greater for high support velocities than for low ones, probably because of the fact that more air is entrained between the support and the free-falling curtain as the speed of the support increases. Means for reducing the air barrier at the surface of the support, e.g., air shields, have been described hereinbefore and are illustrated in the drawings.

In the practice of this invention, the height of the free-falling curtain, i.e., the distance over which free fall occurs, is selected to facilitate attainment of the desired objective of applying an extremely thin coating with extremely uniform thickness. In selecting the optimum height, an important criterion is that the height be made as small as is practical because the longer the free-falling curtain the more susceptible it is to being affected by ambient air currents causing flutter of the curtain and resultant non-uniformity in the product. However, the height must also be selected in accordance with the requirement that the free-falling curtain have adequate momentum at impingement to effectively penetrate or displace the air barrier and adhere to the moving support. To this end, it is desirable that the coating apparatus provide for adjustment of the height of free fall over a substantial range. The air barrier will vary with such factors as the character of the surface to be coated, the effectiveness of mechanical means utilized to remove entrained air, and the velocity at which the support is advanced. Also, since momentum is the product of velocity and mass, if the flow rate of the coating composition is reduced the height of free fall should, in general, be increased so as to increase the impingement velocity and give the free-falling curtain sufficient momentum to penetrate the air barrier. Under typical conditions in the practice of this invention, the height of the free-falling curtain will be in the range from about 5 to about 20 centimeters, but operation at smaller or greater heights than this is also fully within the contemplation of this invention.

Generally speaking, it will be most practical and convenient in the practice of this invention to orient the moving support with respect to the free-falling curtain so that the support moves along a horizontal plane within the coating zone. However, this is not essential and the support can be moved along a path such that the direction of travel is inclined upwardly or downwardly from the horizontal or along a path which is skewed about its longitudinal axis as long as the deviation from horizontal is not so great that the composition flows after coating to render the coated layer excessively non-uniform.

Operation of the method of this invention within the limits hereinbefore described is most readily accomplished by use of the novel coating apparatus hereinbefore described wherein the liquid coating composition

is supported so that it flows as a thin layer along a downwardly inclined slide surface, whereby it is accelerated by gravity at a rate less than acceleration in free fall, just prior to generation of the free-falling curtain. This technique reduces thickness variations within the flowing layer before it falls off the end of the slide surface to form the free-falling curtain and also provides the important advantage that the liquid in the free-falling vertical curtain has very low initial momentum. To render such apparatus useful for handling a variety of photographic coating compositions, it is advantageously provided with means for varying the vertical spacing between the hopper lip and the moving support as well as with means for varying the flow rate of the coating composition and the speed at which the support is advanced. In most instances, it will also be advantageous to provide edge guides to restrain the free-falling curtain and means for reducing the thickness of the boundary layer of air on the surface of the support, as hereinbefore described. The provision of a downwardly inclined slide surface on which the coating composition flows is particularly advantageous where surfactants are added to the coating composition, as it provides adequate time for the surfactant to migrate to the air-liquid interface before free fall begins.

The invention is further illustrated by the following examples of its practice.

EXAMPLE I

Apparatus similar to that shown in FIG. **1** was used to coat aqueous gelatin solutions onto glass plates measuring 25 cm. × 20 cm. and onto sheets of film base and photographic paper measuring 32.5 cm. × 21.5 cm. The hopper used was 37.5 cm. wide and the distance of free fall was 10 cm. Edge anchorage of the longitudinal edges of the free-falling vertical curtain was obtained by means of anodized aluminum plates positioned at right angles to the curtain and extending from the ends of the discharge slot in the hopper down into the catch tray. Three different flow rates and two different support velocities were employed with each of three different aqueous gelatin solutions and, in each instance, a thin uniform layer of the gelatin solution was successfully applied to the surface of the support. Operating conditions employed and the wet coverage obtained are summarized in Table I below.

TABLE I

Coating % Gelatin	Composition Viscosity (cps.)	Flow Rate (cc/sec/cm)	Support Velocity (cm/sec)	Wet Coverage cc/sq. meter
5	6	1.31	305	43
5	6	1.64	305	54
5	6	1.97	305	65
5	6	1.31	457	29
5	6	1.64	457	36
5	6	1.97	457	43
10	20	1.31	305	43
10	20	1.64	305	54
10	20	1.97	305	65
10	20	1.31	457	29
10	20	1.64	457	36
10	20	1.97	457	43
15	43	1.31	305	43
15	43	1.64	305	54
15	43	1.97	305	65
15	43	1.31	457	29
15	43	1.64	457	36
15	43	1.97	457	43

As shown by the data presented in Table I, a given wet coverage can be obtained at any of the coating composition viscosities employed by choosing the proper combination of flow rate and support velocity. This is in marked contrast with bead coating since in the bead coating method at a given web speed the wet coverage will be increased as the viscosity of the coating composition is increased or at a given viscosity the wet coverage will increase in proportion to the web speed. To obtain a lower wet coverage at a given web speed using bead coating it is necessary to reduce the viscosity of the coating composition by diluting it and thereby incur the serious disadvantage of an increased dryring load. As will be apparent, this problem is completely eliminated by use of the method of this invention.

EXAMPLE 2

A hopper similar to that shown in FIG. **1.** having a width of 140 cm. and a 0.025 cm. discharge slot and equipped with wire edge guides secured in the discharge slot 1.9 cm. from each end, was used to determine the effects of flow rate, viscosity, and surface tension on the stability of the free-falling vertical curtain for aqueous gelatin solutions. In each instance, the height of the free-falling curtain was 11.4 cm. For purposes of demonstrating surface tension effects, the aqueous gelatin solutions were tested with and without the addition of surfactants. Results obtained are depicted graphically in FIGS. **13, 14** and **15.** FIG. **13** represents flow rates to which a free-falling curtain which is first established at a high flow rate can be reduced without breaking. FIG. **14** represents flow rates at which the free-falling curtain is resistant to breaking upon introducing a solid object (such as a dry pencil) into the curtain and moving it about. FIG. **15** represents flow rates at which the free-falling curtain will reform of its own accord after being deliberately broken. In each of these figures, surfactant 'A' is saponin at a concentration of 15 per cent in water and surfactant 'B' is a 6 per cent solution in water of an anionic alkyl substituted aryl oxyalkylene ether. Surfactant 'A' was employed at a concentration of 10 cc/liter of gelatin solution and surfactant 'B' at a concentration of 6 cc/liter of gelatin solution. The data presented in FIGS. **13, 14** and **15** demonstrate that viscosity has a significant effect on the flow rate necessary for curtain stability and that, in some instances, there exists an optimum viscosity in this respect. The data also indicate that addition of a surfactant to the coating composition can significantly reduce the flow rate necessary to achieve a given stability in the free-falling curtain.

EXAMPLE 3

A hopper similar to that shown in FIG. **1** was successfully employed to coat a continuous web of film base. The coating composition was a 12 per cent aqueous gelatin solution and it was coated at a flow rate of 1.31 cubic centimeters per second per centimeter of curtain width with the web being advanced at a speed of 430 centimeters per second.

EXAMPLE 4

A hopper similar to that shown in FIG. **1** was successfully employed to coat a web of paper 7.6 cm. in width with a 10 per cent aqueous gelatin solution (28 cps at 40°C) containing 4.5 grams of saponin per 1,000 grams

of solution. The web velocity was 1,000 cm/sec and the wet coverage was 18.8 gms/sq. meter.

EXAMPLE 5

Using a hopper similar to that shown in FIG. **1**, a water solution (9.25 per cent solids and with a viscosity of 120 cps at 40°C) of a copolymer of ethyl acrylate and acrylic acid (a water-soluble synthetic polymer of the type described in U.S. Pat. No. 3,062,674), containing 4.5 grams of saponin per 1,000 grams of solution, was coated on a web of paper 7.6 cm in width. The curtain height was 11.4 cm and the web was advanced at a speed of 900 cm/sec to obtain a wet coverage of 18.8 gms/sq. meter.

EXAMPLE 6

Using coating apparatus similar to that shown in FIG. **12**, photographic coating compositions were satisfactorily coated at web velocities of 38 cm/sec to 1,330 cm/sec, with curtain heights of 2.5 cm to 12.7 cm, and with wet coverages of 16 gms/sq. meter to 150 gms/sq. meter. The coating compositions employed had viscosities within the range of 11 to 120 centipoises and included aqueous gelatin solutions, solutions containing gelatin and polyvinyl phthalate, solutions of a copolymer of ethyl acrylate and acrylic acid, solutions of polyvinyl alcohol, black and white photographic emulsions, and color photographic emulsions.

EXAMPLE 7

A silver halide/gelatin photographic emulsion having a viscosity of 22.5 centipoises was coated on a continuous web of film base by the method of this invention using a slide hopper of the type shown in FIG. **2**. This emulsion is one which when utilized in the bead coating method requires a minimum web velocity of 125 cm/sec and gives a wet coverage at this speed of about 80 cc/sq. meter with skip and mottle problems. Using the method of this invention, at a flow rate of 0.8 cubic centimeters per second per centimeter of curtain width, coating of this emulsion was accomplished without skip and mottle problems and could be successfully carried out at web speeds less than the minimum possible with bead coating. Wet coverages obtained in this test were as follows:

Web Velocity (cm/sec)	Wet Coverage (cc/ sq. meter)
100	80
150	52
200	39

EXAMPLE 8

A hopper of the type shown in FIG. **2** was employed to coat aqueous gelatin solutions with a viscosity of about **28** centipoises onto a continuous web of film base. Tests were made with and without surfactants in the coating composition and results obtained were as follows

Surfactant	Concentration of Surfactant (gms per 1000 cc of solution	Flow Rate (cc/sec/cm)	Web Velocity (cm/sec)	Wet Coverage (cc/sq meter)
None	0	1.05	100	105
'A'	2.65	0.98	100	98
'B'	1.1	0.56	150	37
'B'	3.3	0.66	200	33

These results demonstrate that very low wet coverages can be readily attained by the method of this invention.

EXAMPLE 9

A 15 percent aqueous gelatin solution having a viscosity of 100 centipoises was successfully coated at low web velocities and low flow rates on a continuous web using a hopper of the type shown in FIG. **2** with the lip of the hopper spaced 5.08 centimeters above the web. Results obtained were as follows.

Flow Rate (cc/sec/cm)	Web Velocity (cm/sec)	Wet Coverage (cc/sq. meter)
0.75	50	150
0.56	37.5	150

EXAMPLE 10

A solution of polyvinyl alcohol in water containing 3.4 per cent of the polymer and having a viscosity of 30 centipoises was coated with a hopper similar to that shown in FIG. **2** on a continuous web of paper 9.8 centimeters wide. The flow rate was 1.34 cc/sec/cm and the web velocity was 150 cm/sec to give a wet coverage of 89 cc/sq. meter.

EXAMPLE 11

A 2 per cent aqueous gelatin solution having a viscosity of 2 centipoises at 105°F and containing one gram of surfactant 'B' per 1,000 cubic centimeters of solution was satisfactorily coated on a continuous web using a hopper of the type shown in FIG. **2** under the following conditions:

Flow Rate (cc/sec/cm)	Web Velocity (cm/sec)	Wet Coverage (cc/sq. meter)
0.66	200	33
0.66	100	66
0.54	100	54
0.83	250	33
0.69	250	27
0.59	250	24

EXAMPLE 12

The relationship between coating speed, i.e., support velocity, and wet coverage at a fixed flow rate of coating composition is shown graphically in FIG. **16**, the data having been plotted on logarithmic scales. In this plot, the inclined line AB represents the variation in wet coverage with support velocity at a constant flow rate of 0.56 cc/sec/cm for an aqueous gelatin solution having a viscosity of 40 centipoises applied by the method of this invention to a continuous web of film base. As explained hereinbefore, this flow rate approxi-

mates the lowest flow rate which can be employed with photographic coating compositions and still achieve the necessary curtain stability. The horizontal line AC represents the maximum wet coverage which would be currently useful in the manufacture of photographic elements. The intersection of these two lines, i.e., point A, indicates that the minimum useful support velocity for this flow rate is about 37 cm/sec. For purposes of comparison, the plot includes a broken-line curve representative of conditions under which aqueous gelatin with a viscosity of 40 centipoises can be coated by the conventional bead coating technique. Thus, with bead coating, operation is feasible along the broken-line curve or within the region on the plot above this curve but not within the region below it. Since it is entirely practical to operate in accordance with the method of this invention at any point within the area bounded by the solid lines AB and AC it will be apparent that much lower coverages are attainable for a given coating composition by means of this invention than can be obtained using the prior art method of bead coating. Moreover, it will also be apparent that the method of this invention provides a hitherto unattainable flexibility with respect to choice of operating conditions.

The examples presented hereinabove demonstrate the applicability of the method and apparatus of this invention to the coating of a wide variety of liquid photographic coating compositions and establish that the coated layers obtained are within the required standards with respect to coating thickness and uniformity to render the resulting photographic element useful in the photographic art.

It should be noted that the method of this invention has many important advantages as compared to the bead coating method now in widespread use in the photographic industry. For example, discrete supports can be coated in succession by the method of this invention, whereas bead coating is applicable only to the coating of a continuous support since discrete supports would render it impossible to maintain a stable bead. A further advantage of the method of this invention is that the moving support is spaced at a considerable distance below the lip of the hopper so that splices in a continuous web can pass without detrimental effect and so that the uniformity of thickness of the layer of coating composition applied is not affected by thickness differences or surface irregularities in the support itself. Also, in view of this wide spacing, the problems arising in bead coating as a result of small particles or bubbles being trapped between the lip of the hopper and the support are completely avoided. A further important advantage of the method of this invention is that it permits much greater flexibility in the choice of coating parameters. Thus, for example, in bead coating the speed at which the web can be advanced is dependent on the viscosity of the coating composition and to employ high web speeds it is ordinarily necessary to lower the viscosity of the coating composition by diluting it with water or other liquid. As a consequence, the amount of water which must be removed in the drier is increased and the practical limitations involved in the drying step severely restrict the extent to which coating speed can be increased in this manner. On the other hand, with the method of this invention, the support can be advanced at high speeds using coating compositions of the viscosity ordinarily encountered in the photographic art to provide coated layers of extreme thinness. There is thus no need to dilute the coating composition to go to high coating speeds and the drying problems caused by such dilution in the practice of bead coating are completely avoided.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. Apparatus for coating a layer of liquid photographic coating composition on a continuous web in the manufacture of a photograhic element, said apparatus comprising:

a coating hopper having a cavity for holding said coating composition and a narrow elongated horizontally-disposed discharge slot communicating with said cavity for discharging a substantially uniform thin layer of said coating composition,

means defining a continuous inclined slide surface which adjoins said slot and is disposed to receive on the upper surface thereof the coating composition discharged from said slot and which extends downwardly to a lip; whereby the coating composition discharged from said slot flows by gravity down said slide surface, where it is distributed by the action of gravity to provide exact thickness uniformity across the flowing layer, and over said lip to form a vertical free-falling curtain of coating composition having exact thickness uniformity,

guide means defining edge guide surfaces adjacent each edge of the path of said free-falling curtain for engaging the edges of said curtain to establish the curtain width, said guide means comprising a pair of rods each vertically mounted with the upper end adjacent said lip and the lower end terminating above the plane along which said web is moved and resilient extensions on the lower end of each rod for engaging said web,

means for moving said web along a predetermined path spaced below and transversely of said lip to intercept the free-falling curtain and form on said web a layer of said coating composition, and

shield means depending downwardly from said coating hopper upstream of said free-falling curtain and extending to a position above but closely adjacent the plane along which said web is moved, for protecting said free-falling curtain from air currents and reducing the resistance of the barrier layer of air on the moving web to penetration by said free-falling curtain.

2. Apparatus as described in claim 1 additionally comprising means for varying the speed at which said web is moved.

3. Apparatus as described in claim 1 additionally comprising means for varying the vertical spacing between said lip and said web.

4. Apparatus as described in claim 1 additionally comprising means for rigidly supporting said web as it passes beneath said lip.

5. Apparatus as described in claim 1 additionally comprising a vacuum manifold operatively connected to said shield means for drawing air from the surface of said web.

6. Apparatus as described in claim 1 additionally comprising deflector means mounted to move between

a position where it extends across the path of said free-falling curtain above the path of said web and a position where it is outside the path of said free-falling curtain.

7. Apparatus as described in claim **6** additionally comprising liquid receiving means positioned to receive coating composition deflected into it by said deflector means.

8. Apparatus for coating a layer of liquid photographic coating composition on a continuous web in the manufacture of a photographic element, said apparatus comprising:

a coating hopper having a cavity for holding said coating composition and a narrow elongated horizontally-disposed discharge slot communicating with said cavity for discharging a substantially uniformly thin layer of said coating composition,

means defining a continuous inclined slide surface which adjoins said slot and is disposed to receive on the upper surface thereof the coating composition discharged from said slot and which extends downwardly to a lip; whereby the coating composition discharged from said slot flows by gravity down said slide surface, where it is distributed by the action of gravity to provide exact thickness uniformity across the flowing layer, and over said lip to form a vertical free-falling curtain of coating composition having exact thickness uniformity,

guide means defining edge guide surfaces adjacent each edge of the path of said free-falling curtain for engaging the edges of said curtain to establish the curtain width, said guide means comprising a pair of rods each vertically mounted with the upper end adjacent said lip and the lower end terminating above the plane along with said web is moved and resilient extensions on the lower end of each rod for engaging said web,

means for moving said web along a predetermined path spaced below and transversely of said lip to intercept the free-falling curtain and form on said web a layer of said coating composition,

means for varying the speed at which said web is moved,

means for rigidly supporting said web as it passes beneath said lip,

means for varying the vertical spacing between said lip and said web, and

shield means depending downwardly from said coating hopper upstream of said free-falling curtain and extending to a position above but closely adjacent the plane along which said web is moved, for protecting said free-falling curtain from air currents and reducing the resistance of the barrier layer of air on the moving web to penetration by said free-falling curtain.

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