

Sept. 29, 1970

W. C. KERR ET AL  
TREATMENT OF POLYMER SURFACES FOR COATING  
WITH PHOTOGRAPHIC LAYERS

3,531,314

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2 Sheets-Sheet 1

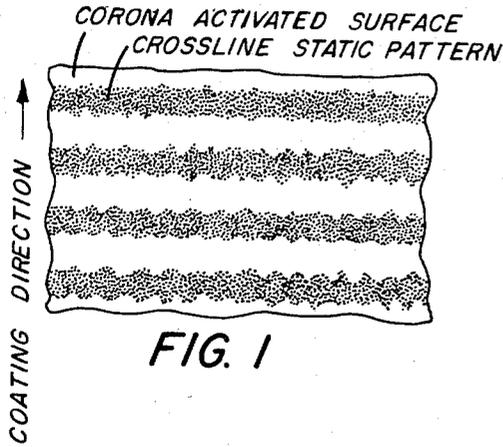


FIG. 1

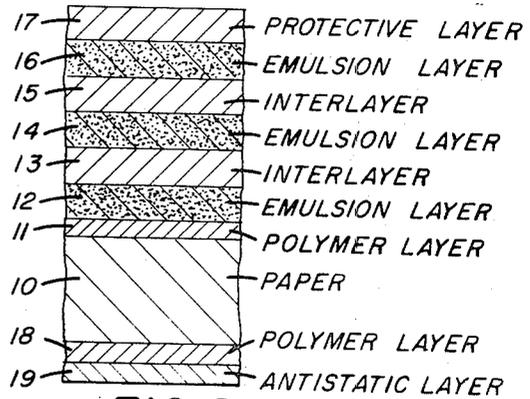


FIG. 2

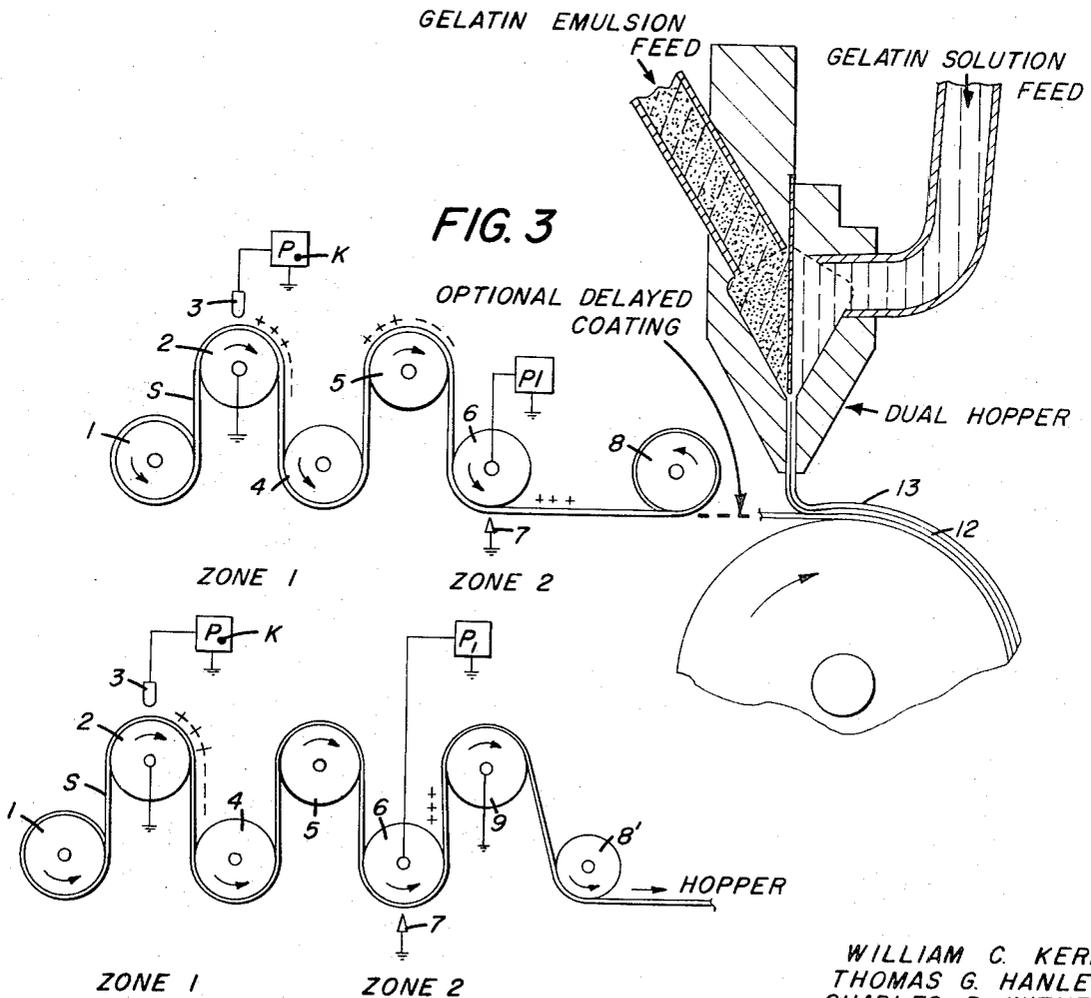


FIG. 3

ZONE 1

ZONE 2

FIG. 4

ZONE 1

ZONE 2

WILLIAM C. KERR  
THOMAS G. HANLEY  
CHARLES R. WITMER  
INVENTORS

BY  
*William C. Jowell*  
AGENT

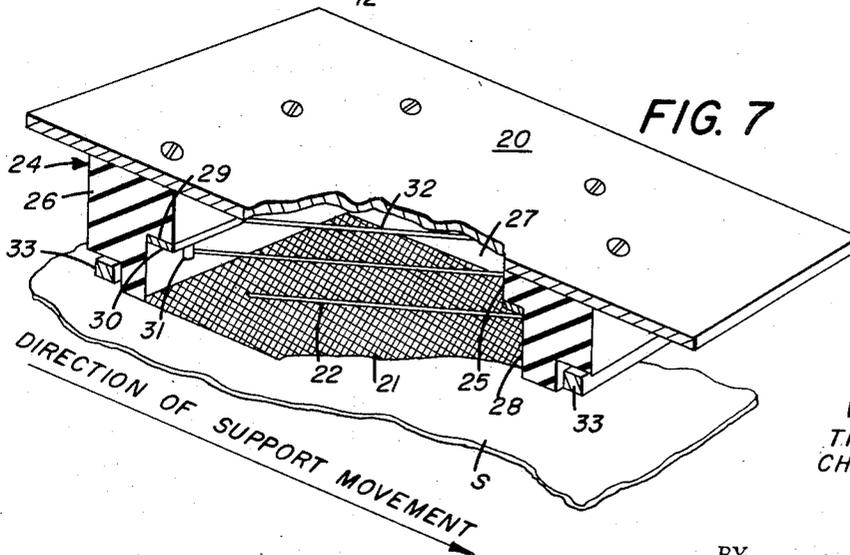
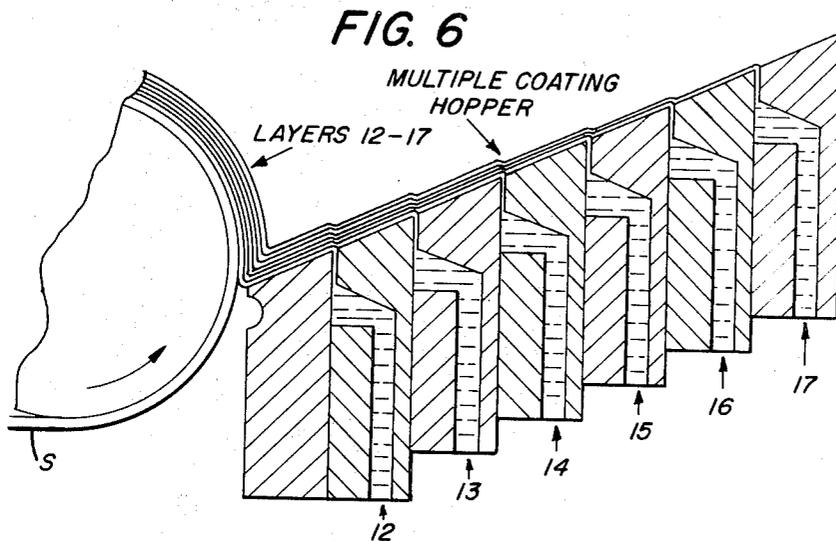
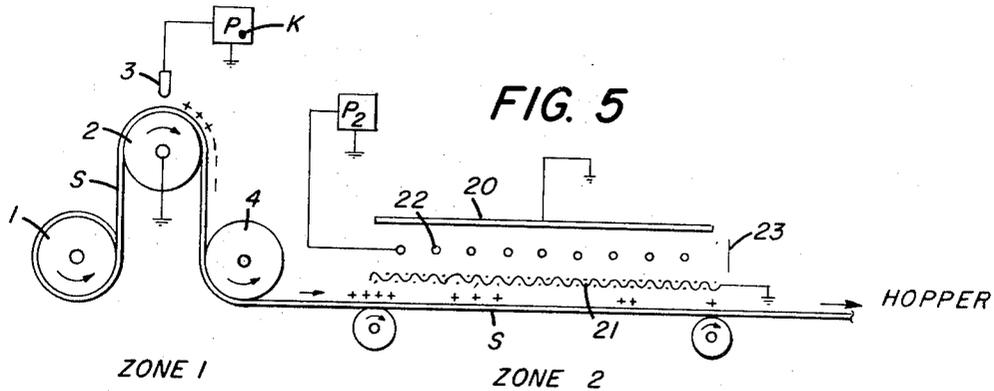
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BY *W. H. M. Jowell*

AGENT

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**TREATMENT OF POLYMER SURFACES FOR COATING WITH PHOTOGRAPHIC LAYERS**

William C. Kerr, Middlesex, and Thomas G. Hanley and Charles R. Witmer, Jr., Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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11 Claims

**ABSTRACT OF THE DISCLOSURE**

Processes for coating photographic layers on polymer surfaces includes corona activation of the polymer surfaces and treatment of the activated surfaces in a DC field to at least reduce the irregularity of the resultant electrostatic charge. Apparatus for intermittent and continuous operation are provided.

Photographic emulsions have been coated on transparent film base or reflective film or paper surfaces for preparation of black-and-white or color images for projection or viewing against the reflective surface for many years. There has long been a need for a waterproof paper support to prevent processing solutions and wash water from penetrating the paper and thus to decrease the washing and drying time of the processed paper prints. Paper coated with organic solvent solutions of synthetic polymers is useful for this purpose but is fairly costly among other disadvantages. More recently, synthetic polymers such as the polyolefins and linear polyesters have been found to be very useful for waterproofing photographic paper and are readily coated upon paper without use of organic solvents, using relatively cheap polymer extrusion methods.

However, as in the case of photographic film base, since the polymer coated paper surface is hydrophobic, the hydrophilic photographic emulsions, especially gelatin-silver halide emulsions, will not adhere unless the polymer surface has been subbed using a composition usually containing a polymer which will adhere to the polymeric paper surface and to which the photographic emulsion layer will in turn adhere. More recently, it has been found that if polymeric surfaces are activated by a strong corona discharge, the photographic emulsions and similar organic colloid layers can be coated with good adherence onto the corona activated polymer surface. This method of adhering the photographic emulsions to the polymer surface materially reduces the cost of manufacture of the waterproof photographic paper but has several serious disadvantages. That is, polymer films, and paper coated with polymers, readily develop static charges during handling and must be provided with antistatic material, particularly when they are to be coated with color emulsion layers. It has been found that the corona discharge in activating the polymer surface of certain supports for adhering the photographic layers, usually leaves an irregular electrostatic charge on the polymer surface. This irregular electrostatic charge causes a defect to appear in the photographic emulsion or other layers coated on the activated surface which has been called "crosslines." FIG. 1 provides a full-scale reproduction of this crossline defect as it appears in a typical gelatin-silver halide emulsion layer or other layer coated on a corona activated polyethylene coated paper surface. The crosslines extend across the sheet. The crossline effect of the corona is so pronounced as to render the corona activated support useless for coating with photographic emulsions since the

crossline pattern is readily visible in prints made on the emulsion layers.

The crossline defect was found to be related to the current frequency of the corona discharge, to chemical and physical properties of the coating compositions and of the support being coated and to mechanical properties and operation of the coating machines. That is, it was observed that when, for example, the surface of a support such as polyethylene coated paper containing antistatic material was activated at about 125 f.p.m. with a corona discharge supplied by an AC current supply of 60 Hz. frequency, the irregular electrostatic crossline charge shown in FIG. 1 was obtained on the activated surface. Similar electrostatic charge patterns were obtained at other corona activation speeds and corona current frequencies. When a photographic layer was coated on the surface, the pattern of the charge on the polymer surface appeared in the coating. In absence of the antistatic material, the charge on the corona activated polymer surface was less intense but indicated the need for a process to reduce the pattern and control the level of the charge on the surface.

The adverse effect of the irregular electrostatic charge on the polymer surface appears to result from the response of the ribbon of photographic coating liquid to the charge on the activated polymer surface as the ribbon is being coated on the surface. A ribbon of coating fluid such as a photographic emulsion being coated on a given coating machine has a significant and measurable vibration frequency and responds to wave energy such as sound waves. On becoming resonant to such wave energy the change in amplitude of the ribbon vibration causes objectionable irregularities to appear in the coating. Such coating ribbons also appear to respond with the wave pattern of the mentioned irregular electrostatic charge on the corona activated polymer surface to cause the crosslines. Different coatings such as very fluid and semi-viscous coatings can be expected to respond differently when coated on different machines. Due to individual characteristics of the coating machines, the same coating made on different coating machines can be expected to respond differently to the same irregular electrostatic charge on the activated polymer surface.

We have discovered that a polymer surface, such as present on polyethylene coated paper, containing antistatic material can be activated with corona discharge for adherence of photographic coatings such as a gelatin emulsion layer, and at least the irregularity of the resulting electrostatic charge obtained on the polymer surface can be reduced, or also the level of the charge on the surface can be controlled to reduce it to a potential such that the coatings can be deposited thereon without adverse effect upon the photographic properties of the coatings. As will be described in more detail below, the methods used for reduction of the irregularity of the electrostatic charge on the activated polymer surface, in one embodiment of the invention, involves modification of the charge on the surface using apparatus such that only light-intensitive layers can be immediately coated on the polymer surface. Other apparatus is used to reduce the irregularity of the electrostatic charge and also the level of charge sufficiently that either light-sensitive or light-insensitive coating can be applied to the activated polymer surface. The processes and apparatus of the invention makes it possible to coat from 1 to 6 or more photographic layers simultaneously onto the corona activated polymer surface with good adhesion and coating uniformity and without adverse effect upon the sensitometric properties of light-sensitive layers.

In FIG. 1 of the accompanying drawings is shown in full-scale the appearance of the mentioned irregular

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crossline electrostatic charge on a corona activated polymer surface when toned with an electrostatic toner. A 60 Hz., 50,000 volt corona measured peak to peak applied at 125 f.p.m. produced this irregular charge on the surface. 400 Hz. corona applied at about 1,000 f.p.m. gives a similar pattern of electrostatic charge on the surface. As mentioned, the photographic layers respond to such electrostatic charge patterns with the result that similar irregularities are obtained in the coated layers. Thus, when a silver halide emulsion layer coated on such electrostatic pattern is developed, alternate areas of different density are visible in the emulsion layer. The electrostatic charge may have a different pattern than shown in FIG. 1 depending, for example, upon the conditions of corona activation, the solutions coated on the activated surface and coating apparatus used.

FIG. 2 shows in greatly enlarged cross-sectional view the appearance of a multilayer photographic element for color photography which is successfully prepared using the methods and apparatus of the invention in the manner described in the examples below by extrusion of polymer layers 11 and 18 upon photographic paper base 10, coating the antistatic layer 19 on the corona activated surface of 18, activating the surface of layer 11 with corona which produces the irregular electrostatic charge on the polymer surface, followed by treatment to reduce the irregular pattern of the electrostatic charge and optionally to substantially eliminate the charge on the surface, and immediately or at a later time coating the emulsion, interlayer and protective layers 12-17 separately or simultaneously on the polymer surface.

FIG. 3 shows in diagrammatic form one method and apparatus of the invention for preparing corona activated polymer surfaces for coating with photographic layers from a hopper of the type shown. Roll 1 is a supply roll for a support S having a polymeric surface which is corona activated at zone 1 which comprises the dielectric coated electrode roll 2 and several electrodes, one of which is shown as the electrode 3 connected to power supply P. Knob K represents a means for regulating the current frequency of the corona discharge. Means for varying the voltage can also be contained in the power supply circuit. An irregular electrostatic charge is formed on the polymer surface. Rolls 4 and 5 serve primarily as transport rolls but if connected to ground may cooperate with the means at zone 2 for reducing the irregularity of the electrostatic charge on the polymer surface. Roll 6 is an electrically conducting electrode such as a steel roll contacting the corona activated surface of the support. Electrode 7 is, for example, a thin wire of, e.g., steel or tungsten or a metal knife electrode spaced from the other surface of the support in opposition to electrode 6 and is connected in circuit to electrode 6 which is connected to a DC supply P<sub>1</sub>, e.g. 5,000-50,000 volts, sufficient to develop an electrical field between the electrodes (usually a corona) through which the support moves, e.g. 50 to 600 f.p.m. or faster to obtain good contact of the polymer surface with electrode 6 and reduce the irregularity of the electrostatic charge on the polymer surface. Electrode 7 may be grounded as shown or have DC supplied to it of polarity opposite that supplied to electrode 6. At slow speed it is possible but less preferred to entirely omit electrode 7 and still obtain useful reduction in irregularity of the charge on the surface. In this case, contiguous machine parts such as an idle roll appear to furnish the ground. Thus, this contiguous machine part is the electrode 7 and replaces a wire or some other type of electrode mentioned above. Roll 8 is a driven windup roll. As a result of operation with this apparatus (as opposed to the process and apparatus of FIG. 4 and FIG. 5 below), an electrostatic charge remains on the support which is substantially uniform but usually has sufficient potential, e.g. 1,000 volts, that when a light-sensitive layer such as a gelatin-silver halide emulsion layer is immediately coated upon the

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activated polymer surface as it leaves roll 6, a discharge occurs which fogs the light-sensitive photographic emulsion. However, if the support is merely wound in the roll 8, the remaining uniform electrostatic charge on the surface is quickly dissipated to below sparking potential and later, e.g. a few minutes to about three days later, one or more photographic emulsion layers such as gelatin and emulsion layer 12 and 13 can be coated simultaneously upon the support using a coating apparatus such as the dual hopper as shown in FIG. 3. Winding the support in a roll after it passes electrode roll 2 of FIG. 3 does not materially reduce the surface charge.

As illustrated in the examples below, the support emerging from zones 1 and 2 carrying the uniform electrostatic charge can, however, be immediately coated with light-insensitive layers such as dyed gelatin layers, gelatin antistatic layers, etc. which are not adversely and in fact may be advantageously affected by the uniform electrostatic charge on the polymer surface. That is, a high uniform charge can be used to stabilize coating ribbons of such materials so that it is possible to coat thin layers at high speeds. For this purpose windup in roll 8 can be omitted and a coating device such as the coating hopper shown is advantageously combined with the apparatus of zones 1 and 2. Thus, the preparation of the polymer surface and its coating can be carried out continuously on the one machine.

The apparatus and process shown at FIG. 4 is similar to that of FIG. 3 except the apparatus at zone 2 of FIG. 3 is modified to include at least one unit means to reduce the irregularity of the electrostatic charge on the surface and also to control the level of electrostatic charge on the polymer surface so that the surface can be immediately coated with photographic layers including light-sensitive layers without adverse effect of any electrostatic charge remaining on the polymer surface. That is, the apparatus at zone 1, FIG. 4, including rolls 1 and 4, electrodes 2 and 3 and power supply P is operated as described above to activate the polymer surface and results in the irregular electrostatic charge on the surface. Zone 2, where the electrostatic charge is modified, includes at least the mentioned electrodes 6 and 7 connected to the DC power supply P<sub>1</sub> and the roll 9 is a conductive electrode, preferably a metal roll, which may be connected directly to ground and which is positioned close to electrode 6 or 7, e.g. 6-12 inches away from electrode 6, but preferably not so close that arcing takes place between the electrodes. The electrical field between electrodes 6 and 7 (usually sufficient to give a corona) is regulated and the distance between the three electrodes adjusted to cause not only a substantial reduction in the irregular pattern of the electrostatic charge but also to control the level of charge on the polymer surface. Thus, substantially all charge can be removed from the polymer surface to leave a surface having 100 volts or less charge having no adverse effect on photographic coatings applied thereto. In some cases it is desirable to alter the action of the apparatus at zone 2, e.g. by connecting electrode 9 to ground through a variable resistance or capacitance or both. Similarly, either or both rolls 5 and 8' can be grounded or their conductive properties varied to produce the desired modification and reduction in level of the electrostatic charge on the polymer surface. Accordingly, apparatus of zones 1 and 2 of FIG. 4 can further include in a single machine, a coating hopper such as shown in FIG. 3 or FIG. 6 to allow continuous treatment of the polymer surface and deposition of one or more photographic layers simultaneously on the polymer surface. However, the apparatus of zones 1 and 2 of both FIG. 3 and FIG. 4 devoid of the coating hopper are valuable to provide product in those cases where for other reasons it is not desirable to immediately coat the photographic layer on the polymer surface. For example, some photographic emulsions useful in layers 12 and 14 of the FIG. 2 element are adversely affected by even a small uniform electrostatic charge remaining on the treated

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polymer surface is activated and the charge obtained on the surface altered using the FIG. 3 or FIG. 4 apparatus and the coating of the sensitive layers on the polymer surface delayed a few minutes to about 48 hours but not so long that the adhesion of the layers to the polymer surface is not acceptable.

The apparatus and process of FIG. 5 are also useful to both reduce the irregularity of the electrostatic charge on the corona activated surface and to control, e.g. eliminate, the electrostatic charge from the surface. Zone 1 comprises the apparatus and process described above for activating the polymer surface and imparting the irregular electrostatic pattern onto the surface. The support then passes from roll 4 into zone 2 comprising at least one apparatus such as shown in detail in FIG. 7 providing a source of ions and which includes adjacent the activated surface of the support, a backing electrode 20, a control screen 21 of metal wire mesh, perforated metal plate, etc. is grounded or held at a selected potential and one side of which is spaced from the electrode 20; several electrodes 22 such as fine steel or tungsten wires are arranged at an angle or directly across the support and between electrode 20 and screen 21 and are connected in circuit with electrode 20 and a current supply P<sub>2</sub> usually AC, of about 10,000 to 20,000 volts or higher. An electrical field comprising negative and positive ions is developed between electrodes 20 and 22, a portion of the ions passing through screen 21 to the charged surface of the support as it passes close to, e.g. 1/2 inch, from the lower surface of the screen at a speed of about 100-150 f.p.m. or higher. As a result, the electrostatic charge on the polymer surface can be substantially eliminated, i.e. reduced below sparking potential, and the support emerging from zone 2 at 23 can be coated immediately or shortly thereafter with photographic layers such as 12-17 of FIG. 2. Accordingly, a machine combining the apparatus of zones 1 and 2 and a hopper such as shown in FIG. 3 or FIG. 6 is advantageously used to continuously corona activate a polymer surface, modify or substantially eliminate the electrostatic charge thereon and for depositing at least one light-sensitive or light-insensitive photographic layer on the polymer surface. This process shown in FIG. 5 is less preferred compared to the processes shown in FIG. 3 and FIG. 4 since the treatment at zone 2 appears to be less effective at the same speeds of treatment because of the limited amount of ions which can be produced in FIG. 5, zone 2 apparatus constructed and operated as described. Accordingly, the FIG. 3 and FIG. 4 processes can be carried out at substantially higher web speeds. The apparatus of FIG. 5, zone 2, can be constructed so as to transport the support from roll 4 over a single large roll and the screen 21, electrode wires 22 and backing electrode are curved around the large roll so the support can travel very close to the screen and the ions more effectively treat the charged polymer surface. Thus, the polymer surface can pass about 1/8 inch from the screen and by use of the higher voltages on the electrode wires, e.g. 20,000 volts or higher, speed of travel can be increased to several hundred feet per minute and still provide sufficient ions to reduce the pattern and level of the electrostatic charge on the polymer surface.

The apparatus and process of FIG. 4 described above can be altered to additionally include the treating means of FIG. 5, zone 2. That is, the FIG. 5, zone 2 apparatus (including backing electrode, screen and plurality of other electrodes) is built into the FIG. 4 apparatus in a third zone following roll 9 of zone 2 so the polymeric surface can pass close to the surface of the screen and the ions passing through the screen can cause any electrostatic charge remaining on the polymer surface to be eliminated. To attain this result a DC potential can be supplied to the electrode wires 22 of polarity opposite that which is supplied to electrode 6. Accordingly, the zone 2 apparatus can be operated so a small uniform electrostatic charge remains on the polymer surface which is removed in the

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zone 3 apparatus. Thus, the zone 2 and 3 apparatus cooperated to both reduce the irregularity of the electrostatic charge and also to control (eliminate) the charge on the surface.

Similarly, following the zone 2, FIG. 4 apparatus, a duplicate zone 2 apparatus may be added (i.e. a second set of parts 5, 6, 7, 9 and P<sub>1</sub>) but in which the polarity of the new power source P<sub>1</sub> has reversed polarity to further reduce the surface charge.

FIG. 6 shows a typical multiple coating hopper useful in the processes described above. The construction and operation of such hoppers is described in detail in U.S. Pat. No. 2,671,791. Thus, solutions for layers 12-17 of the FIG. 2 element are extruded onto the slide surfaces of the hopper and in superposed relation coated simultaneously onto the modified corona activated surface.

FIG. 7 shows the construction of a device useful in the process of the invention at zone 2 of FIG. 5, or following zone 2, FIG. 4, wherein the electrode 20 of metal is screwed to the frame 24. The frame has an opening 25, for example, about 8 inches wide and as long as the width of the support S being treated and of variable width. The members 26 and 27 are provided with an intermediate cut-out portion 28 which forms a shoulder 29 on which a metal strip 30 is mounted and secured by screws not shown. The strip 30 carries a plurality of spaced pins 31 around which a single wire 32 can be strung to form wires 22 which extend transversely or perpendicularly to the direction of movement of support S. The control screen 21 is secured to the bottom of frame 24 or members 26 and 27 by bars 33 which are secured to frame 24 by screws not shown. The screen 21 can be arranged midway between the support S and the backing electrode 20 and the wires 22 can be arranged midway between the screen 21 and backing electrode 20.

Corona activation of the polymer surfaces at zone 1 of the processes illustrated in FIGS. 3, 4 and 5, which produces the irregular electrostatic charges on the surfaces, is conveniently carried out using as a power supply a known spark-gap type power supply which has current supplied to the electrodes by a spark-gap excited oscillator in a well-known manner. Variation in fundamental frequency of the corona is obtained by changing the primary power frequency of the oscillator. A high voltage corona is desirable, e.g. 25,000 to 50,000 volts or higher measured peak to peak, to obtain adequate adhesion of the hydrophilic photographic layers such as gelatin emulsion layers to the corona activated polymer surfaces such as polyethylene. Voltages of this range are adequate for corona activation of polymers at web speeds of about 100 to 1,000 feet per minute or higher. Voltage is varied by spacing the spark-gaps and by varying the primary voltage to the oscillator. Due to the inefficiencies of the spark-gap power supply a continuous wave generator can be used. This sort of waveform generator is available from simple rotating motor-generator sets and frequency control is obtained by speed control of the driving motor. Continuous wave corona is obtained by using as the power source a motor-generator set whereby a sinusoidal waveform generator with a fixed number of poles is driven by a variable speed motor, giving a variable frequency sine wave output. Variation in frequency of the continuous wave corona is obtained by varying the speed of the driving motor. Voltage of the continuous wave corona which is stepped up in value by a multitap transformer and varied by field control can vary from about 5,000 volts to 30,000 volts or higher at web speeds of about 100 to 1,000 f.p.m. The corona can be applied to the polymeric surface of the support, for example, by means of several metal electrodes, one being shown at 3 in FIGS. 3, 4 and 5 positioned close to the polymeric surface at a point ahead of zone 2 where the polymeric surface is passing over a grounded electrode metal roll 3 coated with a dielectric material such as a linear polyester, electrode 3 being connected to power source P having one or more knobs K

used for varying the corona current frequency or voltage. Similarly, a metal roller may be used to support the web with the other electrode array being in planetary disposition equidistant from the surface of the metal roller and each being coated with a dielectric, at least on the surface nearest the metal roller. The spacing of the electrodes to the polymer surface and ground roll should be adequate to produce an activating corona at the voltage used and yet allow for free passage of polymeric sheet through the activating zone. Corona supplied by DC current, or a combination of AC superimposed on DC can be used. However, there appears to be no adhesion advantage in using DC corona and, in fact, AC is preferred since the continuous wave AC corona requires much less power and is, thus, considerably cheaper to use.

The adhesion of the hydrophilic photographic layers to the hydrophobic polymer surfaces after they have been treated with an activating corona and then treated to alter or substantially eliminate the static charge thereon, can be predicted in some cases by measuring the contact angle of the polymer surface. "Contact angle" in degrees is a measure of layer adhesion to the corona activated polymer surface. In the case of polyethylene surfaces, if the corona activated surface has a contact angle of less than about 76°, for example 40° to 75°, dry and wet adhesion of gelatin layers is usually adequate. Contact angle is the contact angle when a drop of distilled water is placed on a level surface of the activated polymer layer. The contact angle is obtained by projecting the image of the drop onto a suitable screen using a contour projector and measuring the angle of a line tangent to the drop image at the point the edge of the drop touches the sample. If desired, a more practical test for adhesion can be made by merely scratching the surface of the coating which has been applied to the activated surface and rubbing the scratched region to estimate the degree of adhesion.

The DC current supplied by power source P<sub>1</sub> at zone 2 of FIGS. 3 and 4 can have a voltage in the range of about 5,000 to 50,000 volts negative or positive at web speeds of about 50-600 f.p.m. or higher. A voltage is preferably used so a corona is obtained between electrodes 6 and 7 spaced as desired. The higher voltages are, in some cases, less desirable especially when a polymer surface, such as polyethylene on a paper base, facing electrode 7 tends to be punctured by the corona discharge.

The voltage applied to electrode wires 22 of FIG. 5 can be about 10,000 to 20,000 volts or higher. Sufficient voltage should be used to produce a corona between wires 22 and the backing electrode 20 to supply as many ions as possible to pass through the screen 21 to control the level of the static charge on the polymer surface.

The photographic elements which are activated with corona as described above include films or surfaces of various polymers usually hydrophobic, including addition and condensation polymers which can be corona activated to effect adhesion of hydrophilic polymer materials such as gelatin. These polymers include polyolefins such as polyethylenes and polypropylenes and ethylene-propylene copolymers, polystyrene, polybutenes, polypentenes, polyacrylic acid esters, linear polyesters and polycarbonates such as polyethylene terephthalates, polyamides such as nylon, cellulose esters, polyacrylonitrile, polyvinylidene chloride and other copolymers of the indicated monomers such as ethylene-vinyl acetate copolymers. Paper and laminated glassine paper coated with these polymers is especially useful. As mentioned above, the invention is particularly useful with these polymeric films, and paper coated with the polymers, when a conductive antistatic compound is incorporated into the element whereby the corona discharge coats with the antistatic material to produce a pronounced irregular electrostatic charge on the polymer surface. As illustrated in the examples below, external antistatic material can be coated on the polymer surface opposite that to be coated with

the photographic emulsion layer. Antistatic material particularly useful in this layer is a mixture of a (1) colloid such as hydroxymethyl cellulose, (2) colloidal silica and (3) either an alkali metal salt of 2,5-naphthalene disulfonic acid, an alkali metal salt of a lower alkyl naphthalene sulfonic acid, and alkali metal salt of the condensation product of formaldehyde and 2,5-naphthalene disulfonic acid, an alkali metal salt of an alkyl aryl polyether sulfonate or an alkali metal salt of a polymeric carboxylic acid. The compound p-(1,1,3,3-tetramethylbutyl)phenoxyethoxyethyl sodium sulfonate is especially useful. Carbon black can also be used in the polymer layers. The antistatic layers are described in more detail in Miller et al., U.S. patent application Ser. No. 594,226 filed Nov. 14, 1966. An internal antistatic material can be incorporated into the polymer support, into the paper or on the surface of paper which is coated with the above polymeric materials or into the polymer layers on the paper. Antistatic materials especially useful for this purpose include salts such as the alkali metal and ammonium salts of the condensation products of an aldehyde such as formaldehyde with naphthalene sulfonic acids, salts such as sodium sulfate and the like salts of organic compounds, organic antistatic agents, such as triethanolamine oleate, triethanolamine stearate and various polyalkylene polyamine derivatives. Oxyalkylene amine derivatives of phosphorous, polyacryloxyalkyl trialkyl ammonium alkyl-sulfate salts, diethanol amine salts of phosphate esters, carbon black and the like may also be used. The above external antistatic layers augment the internal antistatic method for overcoming static problems. Chu et al., U.S. Pat. 3,253,922 describes this method for providing internal antistatic protection to polymer coated papers.

The photographic layers which are coated upon the corona activated polymer surfaces in the manner described above include all kinds of organic colloid layers such as gelatin interlayers, gelatin filter layers and gelatin-silver halide emulsion layers. The silver halide can be, e.g., silver bromide, silver iodide, silver chloride or mixed crystals of these silver halides, e.g. silver chlorobromide. The hydrophilic organic colloid of these layers is preferably gelatin but it may be replaced wholly or in part by known gelatin derivatives, water-soluble polymers such as partially hydrolyzed cellulose acetate, cellulose methyl ether, polyvinyl alcohol, hydrolyzed vinyl acetate copolymers, vinyl acetal-vinyl alcohol copolymers, alkylacrylate-acrylic acid copolymers, etc. Emulsion layers particularly susceptible to the deleterious effects of the corona activated polymer surfaces are the incorporated coupler gelatin-silver halide emulsion layers well known in the art. These emulsions contain colored or colorless non-diffusing cyan, magenta and yellow dye-forming coupler compounds.

Representative elements for color photography shown in FIG. 2 comprise superposed in the desired order on the corona activated surfaces, red, green and blue light-sensitive silver halide emulsion layers containing, respectively, a cyan-forming coupler (e.g. a phenolic compound), a magenta-forming coupler (e.g. a 5-pyrazolone compound) and a yellow-forming coupler (e.g. an open chain ketomethylene compound). Suitable non-diffusing couplers are disclosed in U.S. Pats. 2,407,293, 2,640,776 and 2,956,876. The couplers can be incorporated into the emulsion layers in accordance with well-known procedures, e.g. using coupler solvents as described in U.S. Pat. 2,322,027 to Jelley et al.

The elements of the invention, prepared as described by coating one or a plurality of differently sensitized emulsion layers on the corona activated polymeric surfaces, after exposure to a subject are processed in the usual manner by use of silver halide developing solutions, fixing solutions, etc. The sensitive elements having the superposed incorporated coupler emulsion layers can be exposed to color negatives and processed directly to color

positives by use of conventional developer solutions containing primary aromatic amino silver halide developing agents. Silver images are then bleached and removed along with the residual silver halide leaving the subtractively colored dye images in the layers. It is in this process that it is necessary that the emulsion in contact with the support (and, of course, all emulsions), not be fogged or otherwise adversely affected when coated on the corona activated polymer surface, since fog produces, e.g. yellow stain in highlights and on the borders of the prints.

These multilayer color elements can also be processed by reversal to color positives. Thus, the element is exposed, for example, to a subtractive color transparency, and as usual, developed with a black-and-white developer solution (a so-called MQ developer), the residual silver halide is then rendered developable by fogging with light or using chemical fogging and color developing solution is used to form the positive dye images in the layers. Silver and residual silver halide are removed by known methods leaving the dye images in the layers. In this process a small amount of fog in a layer due to the corona activated surfaces is not as objectionable since dye obtained from the fogged silver halide is present in the shadow areas of the prints where it is not readily visible.

The following examples will serve to illustrate methods and apparatus useful in carrying out the invention.

#### EXAMPLE 1

Photographic paper is tub sized with a gelatin solution of an antistat material such as described above to provide an internal antistat, and is extrusion coated on both sides with polyethylene at about 8 lbs./1,000 sq. ft. The polyethylene surface on the wire side of the paper is corona activated on apparatus such as shown in FIG. 3, zone 1, 60 Hz., 50,000 volt AC corona being developed between electrode 3 and the polyethylene surface after which the activated element passes at 125 f.p.m. into zone 2 for reducing the irregularity of the electrostatic charge obtained on the surface. In zone 2 a 14,000 volt (+) DC current is supplied to electrode 6 which is a bare, steel roll insulated from the machine through its bearings, electrode 7 is a 0.006 inch thick steel wire extending across the machine and arranged about  $\frac{3}{4}$  inch from the surface of and parallel to the bare steel roll comprising electrode 6. Transport roll 5 is a grounded bare steel roll. Other transport rolls are present between rolls 4 and 5. An external antistat layer is immediately coated in a continuous process on the activated polyethylene surface from an aqueous dispersion of hydroxyethyl cellulose (1.3 lbs.), colloidal silica (30%, 140 lbs.) and the compound p-(1,1,3,3 - tetramethylbutyl)phenoxyethoxyethyl sodium sulfate (12 lbs.). A uniform layer of the antistatic composition is thus obtained on the polyethylene surface.

The other polyethylene surface of the face side of the paper is corona activated and treated to modify the electrostatic charge on the polyethylene surface in the same manner in similar apparatus shown in FIG. 3, zones 1 and 2, and which apparatus is attached to the same machine used for treating the first polyethylene surface. The treated polyethylene coated paper has a uniform electrostatic charge on the surface and is merely wound in a roll at 8 to dissipate the charge to below sparking potential, e.g. to 300 volts or less measured with the usual electrostatic field meter, and at once or as long as three days later is coated with layers 12 to 17 of FIG. 1. (When 22,000 volts (+) DC is used on roll 6, one day standing in the roll was useful.) A dual hopper such as shown in FIG. 3 is used for this purpose to apply a blue sensitive gelatin emulsion layer 12 and gelatin interlayer 13 simultaneously to the activated polyethylene surface at about 125 f.p.m. for making a product shown in FIG. 2. The emulsion layer is free of fog and the coatings comprising layers 12 and 13 are uniform. The pairs of layers 14, 15 and 16, 17 are coated similarly to give fog-free uniform coatings. Layers 12, 14 and 16 are gelatin-silver chloro-

bromiodide emulsion layers adapted to reversal color processing and primarily sensitive, respectively, to blue, green and red light and containing, respectively, non-diffusing yellow, magenta and cyan-forming couplers. The emulsions are of the type described in Example 2 of Van Campen, U.S. Pat. 2,596,879. Layers 13, 15 and 17 are gelatin layers. The above process is also successfully carried out supplying current from about 5,000 to 50,000 volts (+) or (-) DC current to roll 6.

The resulting element is exposed to a color original and processed by known reversal color development methods with the result that the mentioned crossline defect illustrated in FIG. 1 does not appear in the positive dye images. The adhesion of the layers to the corona activated polyethylene surface is excellent. When the layers 12-17 are coated in the same manner on the polyethylene surface which has been corona activated at zone 1, but not given the zone 2 treatment, adhesion of the layers to the polyethylene surface is satisfactory but the objectionable crossline pattern of electrostatic charge on the polyethylene surface produces irregularities in the coatings on the polyethylene surface.

When the process of this example is carried out in the same manner using the FIG. 3, zone 1 and zone 2 apparatus, and about 5,000 to 50,000 volts (+) or (-) DC on roll 6, and after winding the polyethylene coated paper in a roll, photographic layers 12-17 are coated simultaneously using a multiple coating hopper such as shown in FIG. 10 of U.S. Pat. 2,761,791, the coating is found to be uniform and free of fog.

#### EXAMPLE 2

This example illustrates another method for at least reducing the irregularity of the electrostatic charge on a 60 Hz. corona activated polymer surface.

The polyethylene coated paper of Example 1 on the polyethylene surface on the wire side is provided with the internal and external antistat materials in the manner described in Example 1. The polyethylene surface on the face side of the paper is treated similarly but continuously in the apparatus shown in FIG. 4 wherein as before rolls 1, 4, 5 and 9 are grounded bare steel transport rolls, roll 6 is also a steel electrode roll insulated from the machine through its bearings. Roll 8' is an idle roll and the paper is advanced by driven rolls farther down the machine. Roll 9 is arranged about 6 inches, measured surface to surface, from electrode 6 which is about  $\frac{3}{4}$  inch from electrode 7. 6,000 volts (+) DC current is supplied to roll 6. The polyethylene surface is activated at 60-110 f.p.m. with the 50,000 volt AC corona in zone 1 and the resulting irregular electrostatic charge on the polyethylene surface is controlled through the presence of the grounded roll 9 arranged close to electrode 7. Measurements of the electrostatic charge on the polyethylene surface at a point following roll 9 shows the presence of charge below sparking potential. The polyethylene coated paper product treated in zones 1 and 2, FIG. 4 as described, is immediately coated with layers 12-17 of FIG. 1. These layers are deposited simultaneously from a multiple coating hopper attached to the same machine such as shown in FIG. 6. The construction and operation of such hoppers is described more fully in U.S. Pat. 2,761,791. Layers 13, 15 and 17 are gelatin layers. Layers, 12, 14 and 16 are, respectively, primarily blue, green and red light-sensitive coupler-containing gelatin-silver halide emulsion layers of the type described in Example 2 of Van Campen, U.S. Pat. 2,956,879 adapted to reversal color processing. The couplers are of the usual non-diffusing type yielding dye images of color complementary to the sensitivity of the emulsion layer in which they are present. The resulting element is exposed to a color original and processed by known reversal color development methods described above to form dye images in the emulsion layers. As a result, the emulsion layers appear to have been uniformly coated and the dye images have satisfactory density and contrast. Adhesion of the emulsion

layers to the corona activated polyethylene surface is also good. In particular, the layer 12 containing the yellow dye images shows little fog or coating irregularities due to any electrostatic charge remaining on the surface of the polyethylene layer 11. Similar results are obtained when speed of the process is 60-110 and (-) 3,500 volts DC is supplied to roll 6.

When the same process is carried out except omitting the treatment at zone 2, due to the irregular electrostatic charge on the corona activated polyethylene surface, the layers coated simultaneously on the surface are not uniform and the blue sensitive layer contains significant fog.

The process described using apparatus such as shown in FIG. 4 is subject to considerable variation. For example, one or more of rolls 4, 5 and 8 may be insulated from the machine to aid in reducing the irregularity of the static charge on the polymer surface and optionally to entirely remove the charge from the surface. Some hydrophobic polymer surfaces such as polyethylene terephthalate can be expected to require stronger AC current treatment at zone 1, FIG. 4, for adhering the hydrophilic photographic layers. The amount and type of any antistat in the support may require more or less DC current at zone 2 than indicated to modify the electrostatic charge on the surface. Electrode 7 can take the form of a wire or a thin brush electrode or knife-edge electrode suitably spaced from roll 6 and cooperating with electrode 9 grounded by suitable means, e.g. through a variable resistance, to obtain effective reduction in irregularity of the charge on the polymer surface. To obtain optimum conditions it is desirable to experiment with each different polymer sheet or paper coated with polymer on each different machine containing the mentioned zone 2, FIG. 4. Thus, the different hydrophilic photographic coating fluids can be expected to respond differently to any residual charge remaining on the polymeric surface after passing zones 1 and 2 of the continuous FIG. 4 process. The speed of treatment in zones 1 and 2 should be regulated first of all so that corona activation at zone 1 is adequate and yet the speed of treatment in zone 2 is not too high to effectively alter the electrostatic charge in zone 2. Positive or negative DC current in the range indicated can be applied to electrode 6.

#### EXAMPLE 3

A laminated glassine paper stock free of antistat material is provided prepared as described in Wood et al., U.S. Pat. 3,260,602. This stock contains two thin layers of glassine bonded by polyethylene and the laminate coated on each surface with polyethylene.

The stock is treated on one polyethylene surface in the manner described in Example 2 in the FIG. 4 apparatus using 60 Hz., 50,000 volt corona at 110 f.p.m. at zone 1 and using 6,000 volts (+) DC on roll 6 at the 110 f.p.m. speed. A 9% aqueous gelatin solution containing Malachite Green dye is coated onto the polyethylene surface to obtain a uniformly colored layer useful on the product for curl control and identification purposes.

The polyethylene surface on the other side of the laminate is activated and treated in the same manner in zones 1 and 2 of the FIG. 4 apparatus to reduce the irregularity of the electrostatic charge imposed on the polyethylene surface by the corona and remove any residual electrostatic charge on the surface. A high contrast lith type of gelatin-silver halide emulsion useful in line and half-tone work is then coated upon the activated polyethylene surface. The emulsion coats uniformly and shows no evidence of fog. Emulsion adhesion is good.

When the same process is carried out omitting the treatment with DC current on roll 6 (FIG. 4), the emulsion layer does not coat uniformly. Also, the green dye layer on the other polyethylene surface shows an irregular pattern corresponding to the irregular charge left on the surface by the corona when the DC roll 6 treatment is omitted for this operation.

#### EXAMPLE 4

A polyethylene coated paper support described in Example 1 containing antistatic material is treated continuously in apparatus shown in FIG. 5 wherein the unit at zone 1 is operated with 60 Hz., 50,000 volt current as in Example 1 but at about 100 f.p.m. to activate the polyethylene surface. After passing roll 4 the paper is advanced through zone 2 apparatus in which an AC current of about 10,000 volts is supplied by power source P to the electrode wires 22. As a result, ions of the cloud of ions produced in the field between electrodes 20 and 22 pass through screen 21 and impinge on the activated polyethylene surface as the paper passes by screen 21 about 1/2 inch from screen 21. The result is that the irregularity of the electrostatic charge imparted to the polyethylene surface in zone 1 is reduced in zone 2. The paper may be wound in a roll but the photographic layers 12-17 of the FIG. 2 element are preferably immediately coated in-line simultaneously onto the polyethylene surface using a multiple coating hopper such as shown in FIG. 6. The layers 12-17 are found to have been coated uniformly on the polyethylene surface and a low level of fog is obtained in the emulsion layers 12, 14 and 16.

#### EXAMPLE 5

The process of Example 2 is carried out except that the apparatus shown at FIG. 4 is modified to include following roll 9, the apparatus shown at FIG. 5, zone 2, in a third zone to control (i.e. reduce) the level of any charge on the polymer surface. That is, the polyethylene coated paper is treated at zones 1 and 2 just as described in Example 2, however, after passing roll 9 the paper enters the zone 3 apparatus and passes close to the screen 21 through which the ions of opposite polarity are passing. In this case, the electrode wires 22 are supplied with DC current of polarity opposite to that supplied to electrode 6. As a result, the zone 2 and zone 3 apparatus function together and the treatment at zone 3 can be regulated so that only a small electrostatic charge remains on the polyethylene surface and the photographic layers can at once be coated onto the surface.

#### EXAMPLE 6

Polyethylene terephthalate film is activated as described in Example 1 using the FIG. 3 apparatus, 60 Hz., 50,000 corona being applied at a speed suitable to cause gelatin layers to adhere. 14,000 volt (+) DC is supplied to roll 6. The treated film is wound in a roll before coating with photographic gelatin layers 12-17 in one operation using a hopper such as shown in FIG. 7. Adhesion of the layers to the film surface is good; they are uniform and free of fog.

In the manner of the above examples the other polymer surfaces can be treated with corona discharge in a first treatment zone as shown in FIGS. 3, 4 and 5 to impart adequate adhesion of hydrophilic colloid layers. The speed of treatment in this zone should be regulated so the desired reduction of the electrostatic charge on the polymer surface is obtained in zone 2. Ordinarily, in an in-line process such as shown in FIG. 4, the speed is advantageously determined by the speed selected for coating the photographic layers onto the activated polymer surface. However, in a process using the FIG. 5 apparatus, since a maximum amount of ions is to be provided in the zone 2 apparatus, the speed required at the selected voltage on electrode wires 22 usually governs the speed of activation in zone 1 and the voltage of the zone 1 corona should be adjusted to effectively activate the polymer surface.

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.

We claim:

1. In a process for the preparation of a polymeric surface of a support for adhering and deposition of a coating on the surface in which the surface is activated by corona discharge prior to coating, the improvement for obtaining greater uniformity of coating, comprising treating the surface of the support in a first zone with an activating corona discharge producing an irregular electrostatic charge on the surface, and treating the activated support in a DC field in a second zone to at least reduce the irregularity of said charge on the surface prior to the coating.

2. The process of claim 1 wherein the support containing antistatic material is advanced continuously along a path through the first and second zones and the second zone comprises a first electrode contacting said surface and a second electrode spaced from the other surface of the support in opposition to said first electrode and connected in circuit to said first electrode, and a DC supply connected to the first electrode to develop an electrical field between said electrodes through which the support moves as it passes through said second treatment zone to at least reduce the irregularity of the charge on the surface, and depositing at least one layer of light-sensitive or light-insensitive coating liquid on the treated surface from a coating device in the form of an unsupported body of coating material.

3. The process of claim 1 wherein the corona discharge is produced by either a spark-gap type or a continuous wave type power supply.

4. The process of claim 1 wherein the polymeric surface is on a paper support and the polymer thereof is polyethylene, polypropylene, an ethylene copolymer or a linear polyester.

5. The process of claim 2 wherein the support containing antistatic material is advanced continuously along a path through the first and second zones and the second zone including at least one treating unit comprising (a) a first electrode contacting said polymeric surface and a second electrode spaced from the other surface of the support in opposition to said first electrode and connected in circuit to said first electrode and a DC current supply connected to the first electrode to develop an electrical field between said electrodes through which the support moves as it passes through said second treatment zone, and (b) in the path following said second electrode and on the same side of the support and in contact with the support of a third electrode connected to ground, the strength of said electrical field and the distance between said second and third electrodes being such that said reduction in irregularity and also control in level of the charge on said surface is obtained.

6. The process of claim 5 wherein a coating hopper is in the path following the second treatment zone to deposit at least one layer of coating liquid onto said treated surface of which at least one layer contains light-sensitive material.

7. The process of claim 2 wherein the coating liquid includes silver halide and is deposited on the surface at a time following the treatment of the surface in the second treatment zone when any electrostatic charge remaining on the surface has been substantially dissipated and does not adversely affect the silver halide.

8. The process of claim 6 wherein the support is polyethylene coated paper and the coatings deposited on a treated polyethylene surface of the support include differently sensitized gelatin-silver halide emulsions containing color-forming coupler compounds.

9. The process of claim 7 wherein the support is polyethylene coated paper and the coatings deposited on a treated polyethylene surface of the support include differently sensitized gelatin-silver halide emulsions containing color-forming coupler compounds.

10. In a process for the preparation of a polymeric surface of a support for adhering and deposition of a coating on the surface in which the surface is activated by corona discharge prior to coating, the improvement for obtaining greater uniformity of coating, comprising treating the surface of the support in a first zone with an activating corona discharge producing an irregular electrostatic charge on the surface, and treating the activated support in a DC field in a subsequent zone or zones to reduce the irregularity and level of said charge on the surface prior to coating.

11. In a process for the preparation of a polymeric surface of a support for adherence and deposition of a coating on the surface in which the surface is activated by corona discharge prior to coating, the improvement for obtaining greater uniformity of coating, comprising treating the surface of the support in a first zone with an activating corona discharge producing an irregular electrostatic charge on the surface, and treating the activated support in a DC field in a subsequent zone or zones reducing the irregularity and substantially eliminating said charge from the surface before coating.

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WILLIAM D. MARTIN, Primary Examiner

W. R. TRENOR, Assistant Examiner

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