

- [54] **PHOTOSENSITIVE AND THERMOSENSITIVE ELEMENTS AND PROCESS FOR DEVELOPMENT**
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- [58] Field of Search ..... **96/48 HD, 63, 36, 96/87 R, 66 T, 119 R, 119 PQ, 60, 64, 66 R, 86 R; 117/237**

[56] **References Cited**  
**UNITED STATES PATENTS**

|           |         |                      |          |
|-----------|---------|----------------------|----------|
| 3,152,904 | 10/1964 | Sorensen et al. .... | 96/48 HD |
| 3,312,550 | 4/1967  | Stewart et al. ....  | 96/63    |
| 3,346,384 | 10/1967 | Gaynor .....         | 96/36    |
| 3,447,927 | 6/1969  | Bacon et al. ....    | 96/87 R  |
| 3,589,903 | 6/1971  | Birkeland .....      | 96/67    |

|           |         |                       |         |
|-----------|---------|-----------------------|---------|
| 3,594,229 | 7/1971  | Kefalas .....         | 117/237 |
| 3,625,693 | 12/1971 | Takehiko Iwaoka ..... | 96/75   |

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[57] **ABSTRACT**

Thermosensitive and photosensitive elements, and a process for the development thereof, are provided which comprise a support, an electrolessly deposited layer of a conductive metal, and a photosensitive layer. Suitable electrolessly deposited layers include nickel, cobalt, and nickel-cobalt alloy. Suitable photosensitive materials include any heat developable or heat-stabilizable materials. Of particular interest are photosensitive elements comprising an electrolessly deposited metal in contact with a diazo composition, a heat developable oxidation-reduction image-forming composition, or a stabilizable print-out emulsion as set forth in Bacon et al., U.S. Pat. No. 3,447,927. Such elements may be developed or stabilized by the application of an electric current to the electrolessly deposited conductive metal, to produce heat.

**16 Claims, No Drawings**

## PHOTOSENSITIVE AND THERMOSENSITIVE ELEMENTS AND PROCESS FOR DEVELOPMENT

This invention relates to a heat developable or stabilizable photosensitive element, and methods for the development thereof. More specifically, this invention relates to a heat developable photosensitive material having an electrically conductive metal layer deposited thereon by electroless deposition.

A wide variety of heat developable materials are known in the photographic area. Exemplary of such materials are elements designed for processing by heat as described in Sorensen et al., U.S. Pat. No. 3,152,904; Morgan et al., U.S. Pat. No. 3,457,075; Stewart et al., U.S. Pat. No. 3,312,550; Yutzy et al., U.S. Pat. No. 3,392,020; Colt, U.S. Pat. No. 3,418,122; and Bacon et al., U.S. Pat. No. 3,447,927.

Electrically conducting layers are frequently incorporated in photographic materials, and especially in electrophotographic materials such as photoconductive and xerographic films. In the areas where the conducting layers are to be grounded or otherwise attached to external circuitry, it is customary to improve the electrical properties and resistance to wear by overcoating with, for example, conducting lacquer compositions containing a high percentage of silver, copper or lead powder. Such topical applications increase film thickness locally and in many instances cause winding and threading problems. Adverse changes in flexibility and in expansion coefficients are further complications.

It is an object of this invention to provide heat developable and stabilizable photosensitive elements which incorporate an electrically conducting layer which may be heated by the passage of electric current through said electrically conductive layers. It is a further object of this invention to provide thermosensitive and photosensitive elements in which a photosensitive emulsion is laminated to or coated over an electrolessly deposited layer of an electrically conductive metal.

It is still further object of this invention to provide a method for the electroless deposition of nickel on photographic materials which may be used to provide a layer which may be heated by electric current in order to develop or stabilize an image-wise exposed photosensitive layer contiguous thereto.

It has been found that a layer of an electrically conductive metal, applied by conventional electroless deposition methods, provides a more stable, adherent, heat-resistant, and wear-resistant conductive surface than materials previously prepared by other methods. When to such a layer a photosensitive and heat developable layer is added, said photosensitive layer may be developed reliably by the passage of electric current. When applied to photographic processes, major advantages of this invention include very short warm-up time, very efficient and uniform heating of the emulsion layer, and simplification of processing equipment, since the resistance can be controlled to allow direct application of line voltage.

The process of this invention presents a highly efficient means for the application of heat to such photosensitive emulsions, in a manner more rapid than the normally used method of bringing such emulsions in contact with a heated shoe of large mass. Additional methods for heat development of such emulsions include such means as heating the image-wise exposed

photosensitive layer by a focused laser beam, as disclosed in Marchant et al., Defensive Publication of application Ser. No. 6955, filed Jan. 29, 1970 and published Aug. 18, 1970 as Defensive Publication No. T877006. Other means of heat transfer which have also been found very useful for heating heat-processable emulsions include the use of an infra-red heater such as, for example, a heated stainless steel bar optionally used in combination with a reflector, if a transparent element is being heated; the use of circulated hot air; or an ultrasonic heater. Such heating methods are comparatively inefficient, and involve the use of extensive controls and/or heating equipment. Such heating methods frequency require excessively long heating periods, such as when using heated air.

It has now been found that a heat developable or stabilizable photosensitive element containing an electrolessly deposited conductive layer, may be developed and/or stabilized by the application of electric current to resistively heat said conductive layer. Electroless deposition provides an extremely uniform and even layer of conductive metal, and does not replicate unevenness of the support element surface as a coating thickness variation. Further, the electrolessly deposited metals have a positive temperature coefficient of resistivity, so that local overheating would tend to increase resistance and reduce local power dissipation, a restraining effect.

This invention is based on the use of electroless plating to provide, on the surfaces of recording materials, thin, strongly adherent and highly conducting metal layers in good electrical contact with pre-existing catalytic or catalyst-generating, electrically conducting layers in the materials. It permits the application of nickel, cobalt, nickel-cobalt alloys, palladium, copper, and certain other metals in thin continuous films which have good chemical stability, high mechanical strength, and excellent resistance to bending stresses and abrasion. Such films are extremely tolerant to rapid heating and the passage of electric current, and will not break down upon the application of an electric current.

The term "electroless" distinguishes a class of chemical plating processes, which operate without externally applied current to form a coherent stratum of metal on a catalytic surface such as nickel, cobalt, rhodium, palladium, or gold, or on certain active (i.e., more electro-positive) metals such as aluminum or iron, which generate the catalytic surface when placed on contact with the plating solution. Since the metal being deposited is a catalyst for the plating reaction, the process is autocatalytic and continues as long as the object remains in contact with the active plating bath. Thus, coating thickness may be reliably controlled by control of coating time, bath concentration, bath temperature, and pH, etc.

The described process is not only useful where a portion of a conducting layer is at an outer surface of the material or can be uncovered to serve as a catalyst or catalyst generator or electroless plating, but it has the further advantage that plating and electrical contact can be achieved even through an electrically insulating porous overcoating, such as a layer of gelatin or similar colloid. Since the process is self-catalyzing, plating will begin to occur on a catalytic or catalyst-generating surface underlying a permeable, insulating layer as soon as the active plating bath penetrates the permeable layer and a continuous metal deposit will build up through the interstices of the porous layer until a conductive

path of metal has been built up from the conductive underlayer to the surface. The generation of conductivity from an underlying layer of a metal which is catalytic for the electroless deposition through an overlying permeable colloid layer is facilitated by a high rate of agitation of the bath and will, of course, take place most efficiently through a relatively thin stratum of colloid.

This method is useful in providing tough, wear-resistant conducting surfaces on appropriate sections of existing conducting layers in recording materials such as photographic or electrophotographic film, to enable dependable contact with external circuitry. The conventional conducting layers present in such materials are frequently quite thin, in order to insure good transparency or for other reasons. If uncovered, for example, by local removal of overlayers so that direct connection is possible by contact, they are often too fragile to resist mechanical damage. If covered, even by a very thin layer of a nonconductor, such as a subbing coat in a photographic material, satisfactory electrical contact will be impossible.

It is preferred to place the conducting layer and the photosensitive layer on the same side of the substrate and in direct contact. It is possible, however, to place the heating layer and the heat-developable layer on opposite sides of a relatively thin and heat conductive substrate. Frequently, the two layers are placed on the same side of the element, but with intervening subbing and/or chemically insulating layers between them.

The combination of advantages which accrue to the described process are not obtained by other procedures for depositing metal films. These are either inoperative with photographic materials or the metal layers resulting are not uniform and continuous and lack adequate adhesion and wear life.

Where the conducting layer to be reinforced is a surface coating prepared by vacuum evaporation, further vacuum evaporation of the same or a different metal onto this substrate does not substantially improve mechanical strength, conductivity, etc. Instead, the conductivity and breakdown potential of such a layer are low and its adhesion and its abrasion resistance poor. However, a hybrid system comprising the described electroless process, using an evaporated layer as the catalyst or as the intermediate for formation of the required catalytic surface, produces a surface coating of good mechanical strength and adhesion, high conductivity and good resistance to electrical breakdown. This embodiment, involving electroless deposition of nickel, cobalt, palladium, or the like, on a catalytic or catalyst-generating surface formed by vacuum evaporation, is useful.

The process provides four main advantages: (1) excellent adhesion of the metal layer to the substrate even when the catalyst is a rather fragile evaporated metal layer; (2) good abrasion resistance with even very thin layers of metals deposited on catalytic surfaces of the photographic material; (3) the capability of providing metal layers in conductive contact with existing conductive layers in the material, either directly or through an intervening permeable layer such as an adhesive substrate, a photographic colloid layer, a pelloid coating or the like; and (4) excellent electrical conductivity and resistance to breakdown.

There are also a number of additional advantages. For instance, coating thickness can be controlled by regulating the temperature and time of application;

uniform coatings are achieved without open spots and the operation of the process is simple, e.g., spray application or immersion is commonly used. Control of deposition parameters also allows one to closely control such factors as resistivity.

Through careful selection of heating conditions, one is able to closely control the temperature of development and duration thereof. Electrical heating means may comprise either direct current or alternating current, applied either directly, through suitable current control means, or by capacitive discharge means.

The process can be extended to include reinforcement of conducting layers which are not catalytic or catalyst-generating by pretreatments which provide a catalyst by chemical treatment of the surface areas where electroless plating is desired. For example, successive treatment with a reducing agent, such as hydrazine or stannous chloride, followed by treatment with palladium chloride will provide a thin palladium deposit which will catalyze electroless deposition or nickel or the like.

One of the advantages of the described method is the excellent adhesion and resistant to heat and abrasion obtained with very thin layers of metal. Conversely, it is possible to maintain these benefits when the thickness is increased far beyond what is ordinarily required for excellent conductivity.

The photographic layers and electrically conductive layers as described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, and the like. In the preferred embodiments superior results are obtained when a film support is used which has a heat distortion temperature of at least 180° C in both the length and width directions. Typical supports which can be used are the heat-set polyesters, for example, polyethylene terephthalates, cyclohexylene-dimethylene terephthalates, for example, as disclosed in Kibler, U.S. Pat. No. 2,901,446, issued Aug. 25, 1959, and the like; high-temperature polycarbonates; high-temperature polyimides, for example those disclosed in Chemical and Engineering News, Aug. 24, 1964, Pages 24-25; and the like.

This invention is broadly applicable to any heat-developable or stabilizable photosensitive materials. The method also has application in providing localized heat for the fusing of xerographic toners. For example, this invention is applicable to photographic elements based on diazonium compounds which decompose under exposure to ultraviolet radiation, photographic elements employing a heat induced color-forming condensation reaction, for example with an aromatic amine, of a free radical produced by exposure to ultraviolet radiation, or an earlier form of photosensitive material containing silver oxalate or the like, which after exposure to ultraviolet is decomposed by heating. A more recently described photosensitive material utilizes a conventional light-sensitive silver halide in conjunction with a reducing agent, the two reacting at light-struck areas in the presence of moisture provided from a hydrated salt under the influence of heat. Another recently described material employs a mixture of organic silver salt and organic reducing agent which by itself forms a coating that is substantially latent

under ambient conditions. The introduction of very small amounts of silver halide or other analogous photosensitive metal salts, either within the mixture or in a contacting separate layer, makes possible the creation of a variable image by exposure followed by heating or by application of a solvent. Still other photosensitive materials to which this invention applies include light sensitive films and papers which form images when exposed to a light source and then uniformly moderately heated, containing minor amounts of photosensitive silver halide catalyst progenitor in catalytic proximity with major amounts of heat-sensitive oxidation-reduction image forming reactants which react more rapidly under the influence of said catalyst. A suitable photosensitive element is one such as taught by Stewart et al., U.S. Pat. No. 3,312,550, issued Apr. 4, 1967, including the combination of at least one silver halide emulsion layer, a 3-pyrazolidone silver halide developing agent and an alkaline substance effective to accelerate development of a latent image in the silver halide emulsion in the presence of the developing agent. In the presence of moisture and heating to temperatures of the order of 50°-200° C, such elements may be rapidly developed.

Many photosensitive and thermosensitive elements have been proposed employing, on a support (a) an oxidation-reduction image forming combination, i.e., a combination of an oxidizing agent (e.g., silver behenate), with a reducing agent, especially a phenolic reducing agent, (b) a so-called catalyst for the oxidation-reduction image forming combination, e.g., photographic silver halide, (c) a binder, such as polyvinyl butyral, and (d) a toner, or so-called activator-toner.

This invention is of particular value in the heat-stabilization of stabilized printout emulsions of the type disclosed by Bacon et al., U.S. Pat. No. 3,447,927, issued June 3, 1969. The silver halide emulsions of said Bacon et al. patent are suitable for use as either a developing-out material, a print-out material, or a direct-print material. This photosensitive material can be exposed to light to form a latent image, heated to high temperatures to repress subsequent photodevelopment of the non-exposed areas, and photodeveloped to produce a stabilized direct print record. U.S. Pat. No. 3,418,122, issued Dec. 24, 1968, to Colt, sets forth the process for preparing visible silver photographic images in a fine grain silver halide photographic print out material such as taught by Bacon et al., said process comprising imagewise exposing said silver halide to form a latent image, heating said exposed silver halide to at least about 300° F to repress printing out of unexposed areas of silver halide and thereafter uniformly exposing said silver halide to light to produce a visible silver image.

The heat stabilized print-out materials set forth in the above Bacon et al. and Colt patents are fine-grain silver halide photographic print-out materials comprising silver halide grains which have trivalent metal ions occluded therein, said grains having being formed in an acidic media, and wherein said silver halide grains have a halogen acceptor contiguous thereto. Said trivalent metals ions are selected from the group consisting of bismuth, iridium, and rhodium. Suitable halogen acceptors are set forth at Column 3, line 55 through Column 6, line 20, of Bacon et al., U.S. Pat. No. 3,447,927.

The extent to which the thermosensitive elements must be heated depends, of course, upon the specific

photosensitive composition employed. Thus, it may be necessary to elevate the temperature of the element to from about 35° C to about 250° C, or even higher. The photosensitive layer must, of course, be employed in conjunction with a substrate capable of withstanding the temperature required to induce a direct visible color change or to repress printing out of unexposed areas of silver halide.

The following examples illustrate the described procedure and elements of this invention. Examples 1 through 5 illustrate procedures for electroless deposition of conducting layers on a suitable substrate, while example 6 through 12 illustrate the application of such electrolessly deposited metal layers in heat developable photosensitive materials.

#### EXAMPLE 1

A direct, electron-recording film comprising in sequence an outer silver-halide emulsion coating, a layer containing a fluorescent pigment, a conducting layer of evaporated nickel and a polyester film support is prepared leaving one-half inch of the nickel coating along the edge bare to permit electrical connections. The metal coating is prepared so as to have an optical density of 0.30. (It is desired to keep the minimum transmission density low to facilitate the examination of the processed film, which is done by viewing from the emulsion side during ultraviolet irradiation to activate the fluorescent pigment.) Three identical sheets of material, each 10 inches long by 4 inches wide with one-half inch stripe of bare, evaporated-nickel conducting coating along one of the long edges of the sheet, are used. One sheet is held as the control. The bare nickel edge on the second sheet is reinforced to an optical density of approximately 2.50 by further local vacuum deposition of nickel, using the same equipment in which the original conductive coating was applied and masking the rest of the surface to prevent deposition in the recording areas. The third sheet is treated by electroless nickel plating to produce the same increase in optical density at the edge, using the exposed evaporated-nickel layer as the catalyst. This is accomplished by rolling the film into a helix with the convolutions separated by a one-eighth-inch thick polyurethane foam pad arranged to cover the emulsion area but not the evaporated-nickel edge. The exposed-metal edge of the roll is then suspended to a depth of about five-eighths inch in an electroless nickeling bath of the following composition:

|                                        |            |
|----------------------------------------|------------|
| Nickelous chloride · 6H <sub>2</sub> O | 30.0 grams |
| Sodium citrate · 5 ½ H <sub>2</sub> O  | 15.0 grams |
| Sodium acetate                         | 5.0 grams  |
| Sodium hypophosphite                   | 10.0 grams |
| Water, to make                         | 1.0 liter  |

The bath is maintained at 195° F. Treatment comprises holding the edge in the bath for 15 seconds, removing for 2 seconds and reimmersing. This cycle is repeated six times to reach a density of about 2.50. The edge is then rinsed in five changes of distilled water and squeezed carefully to remove excess surface moisture as the roll is unwound.

The resistivities of the conducting edges of the three sheets are measured and recorded and a 3-inch length along each edge is then subjected to a standard abrasion test procedure in which a stiff bristle brush is moved repeatedly along the test surface.

TABLE I

Comparison of Electrical Conductivity and Abrasion Resistance of Vacuum-Evaporated and Electrolessly-Deposited Nickel Layers

| Material               | Optical Density | Resistance*(Ohms/Square) |                                |
|------------------------|-----------------|--------------------------|--------------------------------|
| I Control              | 0.30            | Fresh 6000               | After Brushing $2 \times 10^8$ |
| II Evaporated Nickel   | 2.56            | 20                       | $10^4$                         |
| III Electroless Nickel | 2.52            | 5                        | 15                             |
| Reinforcement          |                 |                          |                                |

(\*Resistance values are averages of five readings in different portions of the conductive stripe.)

The results in Table 1 show that both methods of nickeling improve conductivity. However, the evaporated-nickel coating (II) has poor abrasion resistance while the electroless plating (III) adheres well and shows good mechanical strength. In a further standard test in which the film is run repeatedly back and forth in a U-shaped path over a half-inch diameter roller, the electroless deposition proves highly resistant to lifting and cracking whereas the evaporated nickel layer is relatively friable and breaks down under stress.

#### EXAMPLE 2

Three lengths of 5-inch wide xerographic film are prepared by coating a resinuous organic photoconductive layer onto a support comprising a subbed polyester film base overcoated with a conductive layer. A narrow strip of the conducting layer is left uncovered at the edge of the material in each case. In the first length of material, the conducting layer comprises finely divided cuprous iodide in a resin binder. The bare edge is bathed according to the process of the invention in a 0.05 percent solution of palladium chloride for 1 minute at 120° F and rinsed well before the electroless plating step. Reduction of the palladium ion by the cuprous ion generates a film of palladium metal suitable to catalyze electroless deposition. In the second length of the material, the conducting layer is generated by immersing the subbed surface of the polyester base in a 2 percent acidic solution of stannous chloride solution for 1 minute at 160° F, rinsing well and bathing for 1 minute with 0.05 percent acidic solution of palladium chloride at 160° F. The resulting palladium coat is catalytic for electroless deposition and the exposed edge requires no further treatment before plating. The third length of material is prepared with a thin cobalt conducting layer applied over the subbing by vacuum evaporation. This also is directly catalytic for the electroless deposition. An electroless plating of nickel is applied on the bare conducting surfaces of the first and third materials and an electroless plating of palladium on the second using the following baths:

#### Nickel Electroless Plating Bath (pH 10)

|                                      |           |
|--------------------------------------|-----------|
| Nickel chloride · 6H <sub>2</sub> O  | 45 grams  |
| Sodium citrate · 5 ½H <sub>2</sub> O | 100 grams |
| Amonium chloride                     | 50 grams  |
| 28% ammonium solution                | 100 grams |
| Sodium hypophosphite                 | 10 grams  |
| Water to make                        | 1.0 liter |

#### Palladium Electroless Plating Bath (pH 10)

|                                  |           |
|----------------------------------|-----------|
| Tetrammine Palladium II chloride | 5.4 grams |
| Hydrazine                        | 0.3 gram  |
| 28% ammonia solution             | 350.0 ml  |

Ethylenediminetetracetic acid  
Water to make  
(2Na)  
1.0 liter

34.0 grams

Good increases in conductivity are obtained and the electrolessly deposited metal shows excellent resistance to abrasion and loosening with no apparent change in dimension or flexibility.

#### EXAMPLE 3

Two strips of cold-rolled steel 2 inches by 4 inches by one-eighth inch are buffed to a bright finish with fine Carborundum powder and then cleaned thoroughly with detergent and hot water, rinsed, agitated for 2 minutes in 5 percent sulfuric acid solution, rinsed thoroughly and dried. The clean strips are warmed to 40° C, coated with a 1 percent aqueous dispersion of photographic grade gelatin containing saponin as spreading agent warmed to the same temperature. The solution is spread uniformly on one side of the strips which are then drained to remove excess solution and the coatings chilled and permitted to dry. The dry coatings are hardened by 10 minutes' treatment in Kodak SH-1 Formaldehyde Hardening Bath at 25° C, washed for 10 minutes in running water at the same temperature, squeegeed and dried. The coated surface is found to present a high resistance electrically insulating barrier to the underlying metal. One strip is then immersed for half its length in a chemical displacement plating bath comprising 20 grams cupric chloride and 1 ml concentrated hydrochloric acid in 1 liter of aqueous solution, at 21° C. Copper deposits almost instantly in the uncoated areas. After about 30 seconds, some change from a silver-gray to a copper color is observed on the coated side. After 2 minutes' treatment the strip is removed, rinsed thoroughly, squeegeed with a cotton to remove some loose powdery copper from the surface and dried. Using flat metal electrodes, good electrical contact may be made from point to point over all the bare metal surfaces. The gelatin coating still presents a high resistance insulating barrier in the coated area. The edges of the gelatin-coated side of the second strip are masked with one-fourth-inch wide waterproof tape and the strip is immersed in an electroless nickel plating bath of the formula used in Example 1. Treatment is continued at 200° F for 10 minutes with continuous agitation. A nickel deposit is obtained on the bare metal side and edges and in the unmasked area on the coated side. Nickeling is apparent first on the bare metal but, after about 3 minutes, it obvious also on the gelatin-coated side. There is no deposition in the masked areas. Using flat metal electrodes, good electrical conduction is obtained from point to point on the "bare metal" side. Good conduction is also obtained from point to point the surface of the "coated" side and from the surface to the base metal. The nickel electroless bath thus penetrates to the iron surface, activating the metal and then electrolessly depositing on this surface, forming a continuously conducting layer in good electrical contact with the underlying iron.

#### EXAMPLE 4

A lith-type silver halide emulsion is coated on a conducting support comprising a base of 0.007 inch polyester film, a vacuum-evaporated nickel layer of 1.28 transmission density, and a very thin gelatin subbing layer. The film is exposed to a line negative of an elec-

tronic switching configuration and developed to a silver image in Kodak D-85 lith developer. The negative is then fixed, washed and treated in Kodak Etch-Bath EB-1 to remove the silver and gelatin in the exposed and developed regions. The etch bath does not remove the subbing layer sufficiently to establish dependable electrical contact with the underlying palladium layer. The negative is then treated in the electroless nickel bath of Example 2 for 5 minutes at 200° F with continuous agitation. A deposit of nickel forms which is found to be in good electrical contact with the vacuum deposited catalyst layer and to present a mechanically sound, continuous surface for the switching.

A control negative, similarly developed and etched, is treated under the same conditions except that the nickel chloride in the processing bath is replaced with an equimolar quantity of palladium chloride (which does not deposit electrolessly in this formulation) in order to establish that the treatment had not removed the subbing layer. After washing and drying the negative, the undercoating is still insulated from the surface by the subbing.

#### EXAMPLE 5

A 24-inch endless belt of reusable photoconductive film of the kind described in Example 2, having a conducting layer (left bare at the edge) of evaporated nickel is marked off into four 6-inch sections. The first is left untreated as the control. The second is reinforced in the bare conducting area by cobalt electroless deposition using the following bath for 5 minutes at 200° F (pH 10);

|                                        |           |
|----------------------------------------|-----------|
| Cobaltous chloride · 6H <sub>2</sub> O | 30 grams  |
| Sodium citrate · 5 ½ H <sub>2</sub> O  | 35 grams  |
| 28% ammonia solution                   | 100 ml    |
| Sodium hypophosphite                   | 20 grams  |
| Water, to make                         | 1.0 liter |

The third section of film is reinforced along the conducting edge area with a conventional commercial conducting lacquer comprising finely divided silver powder in a resinous dope. The material is brushed on and solidifies as the solvent evaporates. The fourth section is similarly striped using a magnetic recording dope composition which also hardens by evaporation.

On examination, it is found that the cobalt deposit gives better conductivity than the silver paste, and produces no appreciable distortion of the film or change in its dimensions. The silver paste increases the thickness and reduces flexibility of the film. Both the cobalt and the magnetic stripes give satisfactory magnetic recording potential, useful for example for coating the belt of photoconductor for automatic adjustments, etc. The magnetic recording dope, however, increased the thickness of the film appreciably at the edge and being nonconductive, interferes with electrical contact.

The five above examples illustrate the superiority of this method of coating various substrates with an electrically conductive metal. The superiority of the process is evident in the excellent adhesion of the metal layer to the substrate, even when the catalyst is a rather fragile evaporated metal layer; very good abrasion resistance observed with even very thin layers of metal deposited on catalytic surfaces; and the capability for providing metal layers in conductive contact with the existing conducting layers in the material, either directly, or through an intervening permeable layer, such as an adhesive substrate, a photographic colloid layer,

a pelloid coating or the like. Superiority is also evident in the uniformity of resistivity and the ability to conduct an electric current without breakdown.

#### EXAMPLE 6

A stock paper is prepared by electrolessly depositing nickel upon a photographic grade paper. The paper is first sensitized by immersion in a stannous chloride sensitizing solution (1 gram per liter) to complete the activation. After thorough rinsing, the paper is immersed in an electroless nickel bath as set forth in Example 1. Deposition begins almost immediately, and a thin layer of nickel is deposited. The paper stock thus prepared is porous, and in each case all of the fibers throughout the sample appear to be coated with nickel. One sample of this stock paper was tested for electrical conductivity and uniform heating as follows.

A 1.5 by 6-inch strip of material prepared as above, nominally 45 ohms per square resistivity, was measured for surface resistivity between linear contacts 1.5 inches long and 1.5 inches apart, and found to vary from 34 to 54 ohms per square so measured. This sample (a) was clamped at its ends between brass blocks, so that 5 inches of sample were exposed. Line voltage, reduced by a powerstat, was applied, and the voltage across the sample and current through it were recorded. Temperature near the center of the exposed face of the sample was observed with an Ircon 700-C telethermometer. Essentially, the expected positive temperature dependence of resistance of the nickel was observed, i.e., as the voltage was increased the measured current fell short of linear dependence on voltage. Twice during the heating of this sample, the telethermometer was used to observe variation in temperature along the length of the strip. It varied between 96° and 120° C with 45 volts applied; and between 125° and 163° C with 72 volts applied.

#### EXAMPLE 7

A sheet of the stock paper as prepared in Example 6 is laminated to a strip of 3M Type 790 paper (available from 3M Company) by a silicone adhesive; and heated by the application of line voltage through a powerstat, at 92 volts for about 5 seconds. The emulsion develops to a dense black with some unevenness.

#### EXAMPLE 8

A heat developable photosensitive composition is prepared by mixing the following components:

|                                                                                         |         |
|-----------------------------------------------------------------------------------------|---------|
| Gelatin (5% by weight aqueous gelatin solution)                                         | 10.0 ml |
| Saponin (13% by weight aqueous solution)                                                | 1.5 ml  |
| Formaldehyde (10% by weight aqueous solution)                                           | 0.3 ml  |
| Silver nitrate (0.1 molar aqueous solution)                                             | 0.1 ml  |
| Dye * (0.1 percent by weight in methanol)                                               | 2.0 ml  |
| Silver behenate                                                                         | 1.0 g   |
| Methanol                                                                                | 10.0 ml |
| 4-phenylcatechol (10% by weight aqueous solution)                                       | 10.0 ml |
| * 1-carboxymethyl-5-[(3-ethyl-1-(1-benzoxazolidine-ethylidene)-3-phenyl-2-thiohydantoin |         |

A layer of this composition is flow-coated over a sheet of the nickel coated paper as prepared in Example 6.

The resulting photographic element is sensitometrically exposed to tungsten illumination for 5 seconds. The photographic element is then heated by the application of about 32 volts for 10 seconds to the nickel

bearing element. A second sample of this material, identically prepared, was heated by the application of electric current from a charged capacitor. This sample, as well as the first, developed to yield a visible image.

#### EXAMPLE 9

A photosensitive composition is prepared by adding 5 cc

of phenylmercaptotetrazole (1 percent by weight methanol solution) and 5 cc of phthalic acid (2 percent by weight aqueous solution) to a 50 cc solution containing 7.5 percent by weight silver behenate and 3.75 percent by weight polyvinylbutyral in methanol. To this is added 6cc of 3-(dihexylaminomethyl)-5-phenylcatechol hydrochloride (10 percent by weight methanol solution), 6cc of hydroquinone (10 percent by weight methanol solution) and 3 cc of dye, as described in Example 8, (0.02 percent by weight in methanol). The mixture is coated on a nickel-bearing paper support to provide a photographic element.

The resulting element is sensitometrically exposed to tungsten light and then heated as described in Example 8. A visible image is developed.

#### EXAMPLE 10

A heat developable diazonium photosensitive composition is prepared as follows.

|                                                                  |          |
|------------------------------------------------------------------|----------|
| Water-soluble cellulose acetate (10% by weight aqueous solution) | 25.00 ml |
| Cyclohexylsulfamic acid                                          | 0.5 g    |
| p-Diazodiethylaniline zinc chloride                              | 0.25 g   |
| 6,7-Dihydroxy-2-naphthalene sodium sulfonate                     | 0.5 g    |
| Surfactant (10% by weight aqueous solution)                      | 1.0 ml   |
| 1,8-(3,6-dioxaoctane)bis(isothiuronium trifluoroacetate)         | 1.0 g    |

This coating solution is doctor-blade-coated on a nickel-bearing sheet of the stock paper as prepared in Example 6, at 0.004-inch wet thickness. After drying, the resultant photographic element is exposed to a UV source through a high-contrast image pattern until the diazonium salt is decomposed in the light-struck areas. The exposed element is then subjected to electrical heating to 160° C for one minute. A medium purple-brown dye image is formed in previously unexposed regions.

#### EXAMPLE 11

A silver chlorobromide emulsion (5 percent chloride and 95 percent bromide) is prepared in accordance with Example 18 of Bacon et al., U.S. Pat. No. 3,447,927. The emulsion comprises a halogen acceptor, gelatin, and silver halide grains having bismuth occluded therein. The emulsion is coated on a high-temperature heat-resistant polyethylene terephthalate support upon which a sublayer of nickel has been deposited by the method set forth in Example 6. The emulsion is coated at a lay-down of about 350 milligrams per square foot. The coating is then exposed for 4 seconds in a contact printer through a  $\sqrt{2}$  density-increment step wedge. The strip is then placed in contact with an electric current controlled through a powerstat, and heated to about 200° C. for 5 seconds, after which it is photodeveloped for 5 minutes at a distance of 1 foot from a No. 2 reflector photoflood lamp. A visible image is obtained. Similar results are obtained when such an emulsion is coated on Kapton Type H (DuPont) polyimide support, Kodak T-16 Heat Set Polyester support, Kodak K-1 Polycarbonate and glass

supports. Similar results are also obtained, using a capacitive discharge current-regulating means rather than the powerstat unit employed in this example.

#### EXAMPLE 12

To demonstrate the broad applicability of this invention to various heat treatments of photosensitive material, a xerographic paper is prepared as follows.

A 15-foot length of 20-lb. bond paper, 8 inches wide, is provided with a thin water-resistant resin coating on one side, over which is applied a 0.08 transmission density coating of nickel, by vacuum evaporation. A 5-foot portion of the roll is further nickel-coated by vacuum evaporation until a resistance of 45 ohms per square is achieved. A second 5-foot portion is also overnickel-coated to the same conductivity using electroless deposition, as follows: The paper is wound in a loose spiral and treated for 3 minutes at 135° F in a 4-liter beaker containing 3,500 ml of an aqueous solution of 175 grams ammonium chloride, 40 grams sodium hypophosphite monohydrate and sufficient 10 percent ammonia solution to produce a permanent blue color in the solution. The material is agitated by lifting the spiral conformation about 2 inches and immediately letting it settle, at approximately 10-second intervals.

The third 5-foot length of paper is used as a control. All three sections are then identically overcoated with a conventional zinc oxide-resin photoconductive coating. The resulting xerographic materials are compared in a xerographic copying procedure using negative corona charging, exposure to a light image, magnetic-brush development with a developing composition comprising 5 percent of a finely divided black-pigmented, polystyrene-based toner on 80/100-mesh sponge-iron carrier. Electrical contact with the conducting layer underlying the photoconductive layer is provided through two metal clamps, 8 inches in length, which are placed at opposite ends of the sheet. The clamps are provided with minute, toothlike projections to penetrate the photoconductive layer and provide firm contact with the underlying metal coating. Good developed images are obtained in all cases. The electrodes are then attached to a current source and voltage is applied beginning with 25 volts DC and increasing 5 volts every 2 seconds until sufficient heating is produced to soften and fix the toned image.

Upon application of voltage, samples No. 1 and 3 immediately fail. No. 2, bearing the electrolessly deposited nickel, heats to produce a 110° C softening point with 3 to 5 seconds duration, sufficient to fuse and fix the toner.

The invention has been described in considerable 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. A photosensitive element comprising a support bearing an electrolessly deposited layer of electrically conductive metal and a heat developable photosensitive layer.

2. A photosensitive element as set forth in claim 1 wherein said electrolessly deposited layer is selected from the group consisting of nickel, cobalt, nickel-cobalt alloys, palladium, and copper.

3. A photosensitive element as set forth in claim 1 wherein said photosensitive layer comprises silver halide catalyst-forming means and heat-sensitive reactant image-forming means including an organic silver salt oxidizing agent and a reducing agent for silver ions.

4. A photosensitive element as set forth in claim 3 wherein said electrolessly deposited layer comprises nickel, cobalt, or a nickel-cobalt alloy.

5. A photosensitive element as set forth in claim 1 wherein said photosensitive layer comprises a radiation-sensitive metal salt and a light stable oxidation-reduction reaction composition which is capable of being catalyzed into reaction by free metal nuclei initially formed by exposure to radiation.

6. A photosensitive element as set forth in claim 5 wherein said electrolessly deposited layer comprises nickel, cobalt, or a nickel-cobalt alloy.

7. A photosensitive element as set forth in claim 1 wherein said photosensitive layer comprises an oxidation-reduction image forming combination comprising a silver salt oxidizing agent with a reducing agent, a binder, and an activator-toner agent.

8. A photosensitive element as set forth in claim 7 wherein said electrolessly deposited layer comprises nickel, cobalt, or a nickel-cobalt alloy.

9. A photosensitive element as set forth in claim 1 wherein said oxidizing agent is silver behenate.

10. A photosensitive element as set forth in claim 1

wherein said photosensitive layer comprises a direct-print halogen acceptor and silver halide crystals formed in an acidic media with trivalent antimony, arsenic, bismuth, gold, iridium or rhodium ions occluded on the inside of said crystals.

11. A photosensitive element as set forth in claim 10 wherein said electrolessly deposited layer comprises nickel, cobalt, or a nickel-cobalt alloy.

12. A process for the preparation of a photosensitive element comprising electrolessly depositing an electrically conductive metal upon a support and applying thereto a heat-developable photosensitive layer.

13. A process as set forth in claim 12 wherein said conductive metal is selected from the group consisting of nickel, cobalt, nickel-cobalt alloy, palladium, and copper.

14. A process as set forth in claim 13 wherein said photosensitive layer is laminated to said electrically conductive metal.

15. A process as set forth in claim 13 wherein said photosensitive material is heat-stabilizable direct-print silver halide emulsion.

16. A process as set forth in claim 15 wherein said emulsion comprises a halogen acceptor, and silver halide crystals formed in an acidic media with trivalent metal ions occluded therein.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,748,137 Dated July 24, 1973

Inventor(s) Joseph H. Worth, Howard A. Miller and Clyde P. Glover

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 14, "frequency" should read  
---frequently---. Lines 17-18, "electrlessly" should  
read ---electrolessly---. Line 59, "or" should read  
---for---.

Column 3, line 4, "dposition" should read  
---deposition---. Line 40, "mechnical" should read  
---mechanical---.

Column 5, line 5, "variable" should read  
---visible---. Line 60, "being" should read ---been---.

Column 6, line 13, "example" should read  
---examples---.

Column 7, line 28, "resinuuous" should read  
---resinous---.

Column 8, lines 1-4 should read ---

|                                      |                |
|--------------------------------------|----------------|
| Ethylenediminetetracetic acid (2 Na) | 34.0 grams     |
| Water to make                        | 1.0 liter ---. |

Column 8, line 19, after "agent" insert ---and---.  
Line 50, "it" should read ---is---. Line 55, after "to point"  
insert ---on---.

Column 9, line 65, omit "the" after "with."

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,748,137 Dated July 24, 1973

Inventor(s) Joseph H. Worth, Howard A. Miller and Clyde P. Glover

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 12, lines 7-8, "material" should read  
---materials---

In the Claims:

Column 12, line 61, "electrolessly" should  
read ---electrolessly---

Column 13, line 26, "claim 1" should read  
---claim 7---

Signed and sealed this 8th day of January 1974.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

RENE D. TEGTMEYER  
Acting Commissioner of Patents