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EUROPEAN PATENT APPLICATION

⑰ Application number: **78300320.5**

⑤① Int. Cl.²: **G 03 G 5/10**

⑳ Date of filing: **25.08.78**

③① Priority: **25.08.77 US 827603**

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④③ Date of publication of application: **07.03.79**
Bulletin 79/5

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⑥④ Designated Contracting States: **DE FR GB**

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⑤④ **Conductive layer for electrophotographic materials and method of making it.**

⑤⑦ An improved transparent electrophotographic element of a conductive support overcoated with a photoconductive insulating layer. Conductive coatings of the reaction product of a metal salt and phosphorus sesquisulfide are adherently bonded to or embedded into the support material to form a stable conductive support that exhibits excellent light transmission and uniform conductivity throughout the element.

EP 0 001 016 A1

TITLE MODIFIED
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-1-

DESCRIPTION

"CONDUCTIVE LAYER FOR ELECTROPHOTOGRAPHIC MATERIALS".

This invention relates to photographic reproduction and more particularly to a novel conductive layer for electrophotographic materials and processes; namely, processes in which an electrostatic latent image is produced by utilizing the property of photoconduction (i.e., a variable conductivity dependent on the intensity of illumination). The electrostatic latent image may be produced in a conventional exposure operation; for example, by means of a lens-projected image or by contact-printing techniques, whereby a nonvisible electrostatic charge pattern (the so-called electrostatic latent image) is created on a surface, in which pattern the charge density at any point is related to the intensity of illumination obtained at the point during the exposure. The latent image may be developed (i.e., rendered visible) by means of a triboelectric powder or liquid toner. Said powder, such as a pigmented synthetic resin, fixes the resulting visible image by rendering the powder permanently adherent to a support on which the image is desired, for example in suitable cases by heating to soften or melt the powder particles. The liquid toner particles which are washed over the surface are caused to adhere permanently by the drying oil component of the liquid toner.

In electrophotographic processes, the electrostatic

latent image is commonly formed on the surface of a photo-conductive insulating layer carried on a conductive support. For example, material comprising such conductive support and photoconductive layer may be charged by
5 applying a uniform surface charge to the surface of the photoconductive layer. The charge can be applied by conventional means such as corona discharge or the like. The charge is retained due to the substantial insulating character, i.e., the low conductivity, of the insulating
10 layer in the dark. On exposure as described above, the photoconductive property of the layer causes the conductivity to increase in the illuminated areas to an extent which is proportional to the intensity of illumination. This results in a leakage of the surface charge in the
15 illuminated areas while the charge in the unilluminated areas remains. This is what constitutes the aforementioned charge pattern or electrostatic latent image.

Electrophotographic processes have become of increasing importance in recent years, especially in
20 connection with office duplicating processes. Consequently, there has been much interest aroused and much effort has been made to obtain suitable materials for making the conductive support and photoconductive insulating layers used in such copying processes.

25 In recent years, many investigations have been made with respect to the nature of suitable photoconductive materials. Several means are known by which organic support materials can be rendered electronically conductive and, in addition, be transparent, especially in the 50-
30 90% light transmission range in the visible spectrum. These methods include controlled-density, vacuum evaporation or sputtering of metals, sputtering of indium under conditions yielding an indium oxide coating, conversion of a thin copper film to cuprous iodide with
35 iodine, etc. However, each technique is both expensive and difficult to perform in a controlled manner and, in addition, affords conductive coatings that are susceptible to physical damage such as rubbing off or scratching.

In the field of transparent electrophotography many applications of the electrophotographic film entail projection display of the images or copying by some duplication process such as diazo film copying. Obviously, 5 in the aforementioned uses, it is highly desirable to have the light transmission of the conductive layer in the element as great as possible consistent with the level of conductivity required for the film to function properly in its electrostatic processing. Projection 10 images have better contrast and esthetics when the background is light and diazo copying requires less exposure when the minimum density of the element (D_{min}) is low.

Several means of ranking the utility of various transparent conductive coatings have been suggested by 15 defining "figures-of-merit" derived from expressions involving both the percent light transmission and the resistivity per unit area.

However, these figures-of-merit fail to account for the substantial differences in the stability of 20 these ultra-thin conductive films which, in applications requiring long-term use such as updatable microfilm, could make some compositions valueless in spite of high figures-of-merit simply due to slow loss of conductivity on aging. It is well recognized that many of the 25 vacuum-deposited metals used to transparently conductivize dielectric substrates; e.g., aluminum, chromium and nickel are prone to just this sort of deterioration due to oxidation or crystal size changes. The conductive composition of this invention is remarkably stable 30 in both resistivity level and optical transmission by accelerated aging at 60°C. in air.

It is therefore the major objective of the present invention to provide an improved electrophotographic element containing a novel conductive layer.

35 The conductive layer of the invention is characterized by a very low-cost per unit area conductivized, simplified and controlled application of a solution process that results in very little variation in light

transmission as well as excellent conductivity for such an ultra-thin film. In addition, the element exhibits a very high degree of electrical stability due to the lack of oxidation or rearrangement (see Example 4) upon
5 storage. Electrophotographic materials containing this conductive layer therefore exhibit superior shelf life properties.

This invention relates to an improved electro-
photographic material comprising a support with a conduct-
10 ive layer and overcoated with a photoconductive insulating layer. More particularly, this invention relates to an improved conductive layer comprising a layer of the reaction product of a metal salt and phosphorous ses-
quiasulfide adherently bonded to or embedded into a support
15 material. Transparent electrophotographic elements can be prepared by coating a variety of metals such as copper, nickel, gold, tungsten, cadmium and silver on a support material to provide up to 80% transmission at as low as $1 \times 10^5 \Omega$ per square centimeter resistivity (and then
20 overcoating with an organic photoconductive layer).

The electrophotographic elements of this invention are useful in transparent electrophotographic applications. Transparent electrophotographic elements consist of a transparent conductive support material overcoated with a
25 layer of a photoconductor in an insulating binder resin. The organic photoconductor can be any of those well known in the art. A support material is rendered conductive according to this invention by treating a polymeric film support material to a solvent swelling procedure,
30 imbibing it with an anchor agent, air drying the agent, and then treating it with a reducible metal salt.

The organic photoconductors useful according to this invention include any of those well known in the art; including the 2,5-bis (p-aminophyl)-1, 3, 4-
35 oxadiazoles, U.S. 3,189,447; 2-aryl-4-arylidene oxazolones, U.S. 3,072,479; substituted Schiff bases, U.S. 3,041,165;

substituted -p and m phenylenediamines, U.S. 3,314,788 and 3,615,404; and various other compounds.

The support may be any material suitable for use in transparent electrophotographic processes, for example, polyester, polycarbonate, polysulfone, etc., support materials.

The support materials can be rendered conductive by a simple inexpensive process that requires only the use of tank baths to form the conductive coating.

10 In the first step of the process, the support is treated with phosphorus sesquisulfide. The phosphorus sesquisulfide can be utilized as a liquid or dissolved in a solvent. Suitable solvents for the phosphorus sesquisulfide are solvents that dissolve the phosphorus
15 sesquisulfide and which preferably swell the surface of the support without detrimentally affecting the surface of the support. In an alternative procedure, a support can first be treated with a solvent to swell the support and then treated with phosphorus sesquisulfide in a
20 second bath. Suitable solvents include the halogenated hydrocarbons and halocarbons such as chloroform, methyl chloroform, phenyl chloroform, dichloroethylene, trichloroethylene, perchloroethylene, trichloroethane, dichloropropane, ethyl dibromide, ethyl chlorobromide,
25 propylene dibromide, monochlorobenzene, monochlorotoluene and the like; aromatic hydrocarbons such as benzene, toluene, xylene, ethyl benzene, naphthalene and the like; ketones such as acetone, methyl ethyl ketone, and the like; acetic acid; acetic acid-trichloroethylene mixtures;
30 carbon disulfide; and the like.

When a solution of phosphorus sesquisulfide is employed in the process, the solution concentration is generally in the range from about 0.0001 weight percent of phosphorus sesquisulfide based on the weight of the
35 solution up to a saturated solution, and preferably from about 0.5 to about 2.5 percent. Prior to contacting the substrate with the phosphorus sesquisulfide, liquid

or solution, the surface of the support should be clean. When a solution is used, the solvent generally serves to clean the surface. A solvent wash may be desirable when liquid phosphorus sesquisulfide is employed. The phosphorus sesquisulfide treatment is generally conducted at a temperature below the softening point of the support, and below the boiling point of the solvent. Generally, the temperature is in the range of about 0° to 135°C, but preferably in the range of about 15° to 75°C. The contact time varies depending on the nature of the support, the solvent and temperature, but is generally in the range of about 1 second to 1 hour or more, preferably in the range of about 1 to 20 minutes.

As a result of the first treatment step, the phosphorus sesquisulfide is deposited at the surface of the support. By this is meant that the phosphorus sesquisulfide can be located on the surface, embedded in the surface and embedded beneath the surface of the support. The actual location of the phosphorus sesquisulfide is somewhat dependent on the action of the solvent on the surface of the support.

Following the first treatment step, the support can be rinsed with a solvent, and then can be dried by merely exposing the support to the atmosphere, or by drying the surface with radiant heaters or in a conventional oven. Drying times can vary considerably, for example, from 1 second to 30 minutes or more, preferably 5 seconds to 10 minutes, more preferably 5 to 120 seconds. The rinsing and drying steps are optional.

In the second treatment step, the phosphorus sesquisulfide treated support is contacted with a solution of a metal salt which is capable of reacting with the phosphorus compound to form the conductive coating on the support. By metal salt, I mean either a metal salt or a metal salt complex. The metals generally employed are those of Groups IB, IIB, IVB, VB, VIB, VIIB, and

VIII of the Periodic Table. The preferred metals are copper, silver, gold, chromium, cadmium, and the like.

The metal salts that are used in the invention can contain a wide variety of anions. Suitable anions include the anions of mineral acids such as sulfate, chloride, bromide, iodide, fluoride, nitrate, phosphate, chlorate, perchlorate, borate, carbonate, cyanide, and the like. Also useful are the anions of organic acids such as formate, acetate, citrate, butyrate, valerate, caproate, stearate, oleate, palmitate, dimethylglyoxime, and the like. Generally, the anions of organic acids contain 1 to 18 carbon atoms.

The foregoing metal salts are used in ionic media, preferably in aqueous solutions. However, nonaqueous media can be employed such as alcohols, for example, methyl alcohol, ethyl alcohol, butyl alcohol, heptyl alcohol, decyl alcohol and the like. Mixtures of alcohol and water can be used. Also useful are ionic mixtures of alcohol with other miscible solvents of the types disclosed hereinbefore. The solution concentration is generally in the range from about 0.1 weight percent metal salt or complex based on the total weight of the solution up to a saturated solution, preferably from about 1 to about 10 weight percent metal salt or complex. The pH of the metal salt or complex solution can range from about 4 to 14, but is generally maintained in the basic range, i.e., greater than 7, and preferably from about 10 to about 13.

The step of contacting the phosphorus sesquisulfide treated substrate with the solution of metal is generally conducted at a temperature below the softening point of the substrate, and below the boiling point of the solvent, if one is used. Generally, the temperature is in the range of about 30° to 110° Centigrade, preferably from about 50° to 100° Centigrade. The time of contact can vary considerably, depending on the nature

of the substrate, the characteristics of the metal salts employed and the contact temperature. However, the time of contact is generally in the range of about 0.1 to 30 minutes, preferably about 5 to 10 minutes.

5 In an alternative embodiment, the first step of rendering a support material conductive, as explained above, can be eliminated by the application to a support of a subbing lacquer containing a solution of phosphorus sesquisulfide. In this embodiment, the conductive layer
10 is formed as a distinctive overcoat on the support material and the imbibing step (step one), as described above, is thereby eliminated. The overcoated support material containing the phosphorus sesquisulfide can then be treated with a metal salt or complex of a metal salt,
15 as described above in the step two treatment, to form the conductive layer on the support material.

 In yet still another and preferred embodiment, a support material such as a polyethylene terephthalate film support is first overcoated with a bond coat and is
20 then treated in the appropriate coating baths in the two step conductivizing procedure as explained hereinbefore. The use of a prebonded (subbed) support has the advantages of affording greatly improved adhesion of the photo-conductive overcoat to the conductive layer as well as
25 improving the uniformity and facility with which the conductivizing is accomplished on the subbing layer versus the unbonded polyester surface.

 In the preparation of the photoconductive layer of the element according to this invention, a photoconductor
30 and a sensitizer are employed in association with a resin or synthetic polymer, for example; natural resins, synthetic resins (including copolymers) such as the polystyrenes or polystyrene copolymers including styrene-butadiene, styrene-butadiene-acrylonitrile; acrylates,
35 polyvinyl acetals, polycarbonates, polyphenylene oxide, phenoxy resins, polysulfones, polyesters and other

synthetic polymeric resinous materials.

The photoconductor compound or mixture is typically employed in an amount equivalent to from about 0.01 to 200 or more percent by weight with respect to the resinous binder. The actual amount of photoconductor to be employed will depend upon the system in which the element is being utilized, i.e., the particular light source, the length of exposure, the particular photoconductor compound being used, etc.

The photoconductive elements containing a photoconductive layer coated on a conductive support of the present invention are usually charged positively or negatively by means of a corona discharge. The light sensitivity of the thus obtained photoconductive element lies mainly in the range of 300-700 nm. Very good images may be obtained by a short exposure using a positive or negative to a conventional electrophotographic light source such as a high pressure mercury vapor lamp, tungsten lamp, laser, xenon flash or the like.

The latent image so produced may be developed in known fashion by the application of a dry powder or liquid toner.

The following examples are merely illustrative and are not deemed to be limiting.

EXAMPLE 1.

A polyethylene terephthalate support is immersed in a solvent solution of tetrachloroethane and phenol in a 80/20 weight ratio in order to open or swell the surface of the support. The solvent swelled support is then immersed in a 2% by weight solution of phosphorus sesquisulfide in tetrachloroethylene at 60°C. for 4 minutes. The support is then rinsed in tetrachloroethylene and then dried by a warm air (60-80°C) flow for 4 minutes. The support is then immersed in an aqueous copper tartrate solution for 5 minutes following by an aqueous rinse and drying for 5 minutes. The support which is visibly

transparent is then overcoated with a photoconductor layer of the following composition:

25% by weight of N, N, N', N'-tetrabenzylmetaphenylenediamine photoconductor and 1/200th (based on the amine) moles of ethyl-violet sensitizer dye are dissolved in a 2:1 polymer solution of acrylic ester and vinyl chloride-vinyl acetate copolymer. The photoconductive layer is applied at a coating weight of approximately 2.5 lbs. per 1000 sq. ft. of substrate which yields a thickness of about 12 microns.

Electrophotographic evaluation using a standardized charging and exposure cycle showed the sample to perform excellently compared to a control of exactly similar design except for use of an aluminum conductive layer having only 55% light transmission versus 70% for the above sample.

	Sample	Corona Sign	Initial Surface Voltage	Voltage Drop one sec after exposure	Dark Decay Rate
20	Control	-	1070	265	8 v/sec.
	Example 1	-	1020	245	35

EXAMPLE 2

A polyethylene terephthalate support is immersed for 2 minutes in a solution containing 2 percent by weight phosphorus sesquisulfide in a solvent mixture of perchloroethylene, trichloroethylene and ethanol at 70°C. The support is then rinsed and dried. The support is then immersed for 10 minutes in a solution of copper pyrophosphate at 60°C. The transparent conductive support is then overcoated with a layer of the following photoconductive composition:

25% by weight of N, N, N', N' tetra B-phenylethyl metaphenylenediamine and 1/200th (based on the amine) moles of ethyl violet sensitizer dye dissolved in a polyester matrix based on phenylindane dicarboxylic acid

and aliphatic diols. The photoconductive layer is coated to yield a dry film thickness of approximately 12 microns.

Electrophotographic evaluation using a standardized charging and exposure cycle showed the sample to perform excellently compared to a control of exactly similar design except for use of an aluminum conductive layer having only 55% light transmission versus 70% for the above sample.

Sample	Corona Sign Charge	Initial Surface Voltage	Voltage Drop one sec after exposure	Dark Decay Rate
Control	-	1090	425	7
Example 2	-	1115	425	90

15

EXAMPLE 3

A prebonded (subbed) polyethylene terephthalate support, Celanar 4521, is immersed in a solvent solution of tetrachloroethane and phenol in an 80/20 weight ratio in order to open or swell the surface of the support.

The solvent swelled support is then rinsed with tetrachloroethane and immersed in a 2% by weight solution of phosphorus sesquisulfide in tetrachloroethylene and dried by warm air (60-80°C) for 4 minutes before being immersed in an aqueous copper tartrate solution for 5 minutes.

After a water rinse, the sample is dried for 5 minutes.

The support which is visibly transparent (80% transmission) and conductive ($60 \times 10^4 \Omega / \text{cm}^2$) is then overcoated with the photoconductor layer of Example 1.

Electrophotographic evaluation using a standardized charging and exposure cycle showed the sample to perform excellently compared to a control of exactly similar design except for use of an aluminum conductive layer having only 55% light transmission versus 80% for the above sample.

Sample	Corona Charge	Initial Surface Voltage	Voltage Drop one sec after exposure	Dark Decay Rate
Control	-	1070	265	8 v/sec
5 Example 3	-	1080	265	50
Control	+	1090	300	10
Example 3	+	1095	247	18

EXAMPLE 4

The excellent stability of the conductive coating was demonstrated through an accelerated aging test wherein the conductivised coating of Example 3 was held at 60°C in a forced draft oven for three weeks and the optical transmission and surface resistivity determined periodically.

	Time-days	% Transmission	Resistivity in Ω / cm^2
15	0	68	3.2×10^4
	1	68	2.7×10^4
	3	70	3.2×10^4
	4	70	3.4×10^4
20	12	70	4.3×10^4
	15	70	5.0×10^4
	21	72	5.5×10^4

CLAIMS

1. A transparent electrophotographic element comprising a support with a conductive layer overcoated with an insulating photoconductive layer, characterised
5 in that the conductive layer is the reaction produce of a metal salt and phosphorus sesquisulfide adherently bonded to the support.
2. An element according to claim 1 characterised in that said metal is selected from the Groups IB,
10 IIB, IVB, VB, VIB, VIIB and VIII of the Periodic Table.
3. An element according to claim 2 wherein the metal is selected from copper tungsten cadmium and silver.
4. An element according to any one of the
15 preceding claims, characterised in that the support is selected from polyethylene terephthalate, polycarbonate and polysulfone support materials.
5. An element according to any one of the preceding claims, characterised by a polyethylene
20 terephthalate support bearing the reaction product of a metal salt and phosphorous sesquisulfide adherently bonded thereto and overcoated with an insulating photoconductive layer.
6. An electrophotographic element according
25 to any one of the preceding claims, characterised by a polyethylene terephthalate support bearing a copper-phosphorous-sulfur layer adherently bonded thereto and overcoated with an insulating photoconductive layer.

7. A method of making a transparent electro-
photographic element, as claimed in claim 1, characterised
by treating a support with phosphorus sesquisulfide and
a solution of a metal salt or metal salt complex and
5 applying an insulating photoconductive layer.



European Patent
Office

EUROPEAN SEARCH REPORT

0001016
Application number

EP 78 30 0320

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<u>US - A - 3 709 727</u> (G.T. MILLER) * Claims 11-16; abstract; column 1, line 65 to column 4, line 75; examples 13-16 *	1-4	G 03 G 5/10

	<u>US - A - 3 681 511</u> (G.T. MILLER) * Claims; abstract; column 1, line 45 to column 7, line 21; examples 17-19 *	1-4	

A	<u>GB - A - 1 452 737</u> (HOOKER CHEMICALS) * Claims *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. ²) G 03 G 5/10

A	<u>US - A - 3 407 093</u> (N. MASUDA) * Claim *	1	

A	<u>DE - A - 1 914 957</u> (KODAK) * Claims; page 5, paragraph 4 to page 11, paragraph 1 *	1	

			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
The Hague	04-12-1978	VANHECKE	