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3,464,820

ELECTROPHOTOGRAPHIC ENGRAVING PLATE
Michael Michalchik, Setauket, N.Y., assignor to Fairchild
Camera and Instrument Corporation, Syosset, N.Y., a
corporation of Delaware

No Drawing. Continuation-in-part of abandoned applica-
tion Ser. No. 451,629, Apr. 28, 1965. This application
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9 Claims

ABSTRACT OF THE DISCLOSURE

An anchor coat for use in the preparation of recording elements such as are used in the preparation of lithographic plates. The anchor coat is a mixture of a Werner complex and a drying agent which is a cobalt, zinc, lead, manganese, iron or calcium salt of naphthenic, octoic or tallic acid.

RELATED APPLICATION

This application is a continuation-in-part of copending patent application Ser. No. 451,629, filed Apr. 28, 1965, and now abandoned.

BACKGROUND OF INVENTION

This invention relates to the improvements in the production of relief images. More particularly, it relates to improvements in the production of relief images by a process which includes the production of a solvent resistant polymeric image. It relates also to compositions useful in the production of such images.

There are a number of commercial operations in which it is necessary or convenient to prepare a relief image which accurately reproduces the original subject. Photoengraving is one such operation. Still another is the production of printed circuits for electrical devices. For convenience, and ease of understanding, this invention will be described as it applies to photoengraving, but it should be understood that the invention is also applicable to other processes where a relief image is necessary or useful.

Recently a procedure has been developed which permits the production of a relief image by a novel process. In this procedure as applied to photoengraving, a recording element is first produced by coating a plate of etchable metal, such as zinc, magnesium, or aluminum, with a coating composition comprising an electrically insulating binder film in which the photoconductive materials include for example, the oxides, sulfides, iodides, selenides and tellurides of zinc, mercury, aluminum, antimony, bismuth, cadmium and molybdenum; metallic lead and selenium; arsenic trisulfide and cadmium arsenide. By far the most widely employed photoconductive substance is zinc oxide. Photoconductive zinc oxide generally has a surface conductivity of at least about 10^{-9} ohm/square/watt/cm.² when exposed to a wavelength of 3900 Angstrom units. The coating is then made sensitive to light by substantially covering the surface with an electrostatic charge. One convenient method of charging is exposing to the surface to be charged a corona discharge produced in any convenient manner. The charge on the surface of the recording element is usually from about 300 to about 600 volts.

The recording element now sensitive to light is exposed to light by any of the conventional processes and the charge is selectively leaked from the surface. The degree of charge decay on a particular area of charged surface of the recording element is directly proportional to the

amount of light to which the area is exposed. If light is projected to the charged surface through a photographic negative, the largest amount of charge decay will be in the area of the recording element corresponding to the most transparent areas of the film. Charge decay in other areas will be correspondingly less depending upon the transparency of the corresponding areas of the film. There is thus produced a latent electrostatic image on the surface of the recording element which accurately reproduces the surface of the recording element which accurately reproduces the negative image on the film. The selective charge decay for the purpose of producing a latent electrostatic image may be effected by other procedures well known in the art.

The insulating film in which the photoconductive material is suspended is a polymeric substance which is capable of polymerization to produce a high molecular weight polymeric product. A number of binder materials have been used in the past and these are suitable for use in this invention, although silicone resins are generally preferred. These include for example, polystyrene; acrylic and methacrylic derivatives of acrylic and methacrylic acids, both supplied by Rohm & Haas Company; Lucite 45, and Lucite 46, polymerized, butyl methacrylates supplied by E. I. du Pont de Nemours & Company; chlorinated rubber such as Parlon supplied by The Hercules Powder Company; vinyl polymers and copolymers such as polyvinyl chloride, polyvinyl acetate, etc., including Vinylite VYHH and VMCH manufactured by the Bakelite Corporation; cellulose esters and ethers such as ethyl cellulose, nitrocellulose, etc.; alkyl resins such as Glyptal 2469 manufactured by the General Electric Company; Rezyl 869, a linseed oil-glycerol alkyd provided by American Cyanamid Company; silicone resins such as DC-801, 804 and 996, all manufactured by the Dow Corning Corp.; or SR-82 a methyl phenyl polysiloxane mixture available from General Electric Company. This latter silicone resin is especially effective in admixture with ethoxylated phenyl siloxanes, for example R-830, available from Union Carbide Corp. Mixtures containing one or more of the above-mentioned binders, or others, may also be employed.

In the next step of the process, the latent electrostatic image is converted to a polymeric image by controlled polymerization of the areas of the insulating film which have retained a charge. This is accomplished by depositing a polymerization catalyst such as finely divided aluminum octoate or resinate on the areas of the recording element bearing the electrostatic image. Deposition may be effected for example by immersing the recording element in a liquid carrier in which the catalyst is suspended. The liquid is characterized by a high electric resistivity and is usually an aliphatic hydrocarbon or an aliphatic halogenated hydrocarbon, or a mixture of these. The catalyst particles, by a process which is not completely understood but is probably a triboelectric phenomenon, acquire relative to the surface of the recording element and are, therefore, attracted to the electrostatic image and deposited on it.

The recording element with the catalyst selectively deposited on its surface is removed from the developer bath, i.e., the carrier liquid with the suspended catalyst and rinsed. The purpose of the rinsing is to remove any catalyst particles which have been deposited on the surface of the recording element in areas other than those bearing the electrostatic image. These randomly disposed catalyst particles apparently deposit as a result of the relatively small electric potential which remains in background areas of the insulating film after production of the electrostatic image. Unless they are removed, they will cata-

lyze extraneous, undesirable polymerization in the background areas. For some applications where high quality reproduction is not essential, this step may be omitted.

After rinsing, the recording element is placed in a curing oven where heat polymerization of the catalyzed area produces a polymeric image corresponding to the original electrostatic image. The polymeric image comprises areas of high molecular weight solvent resistant polymers surrounded by background areas of low molecular weight solvent sensitive polymers. The background area may therefore, be selectively dissolved to expose the metal surface which may be etched according to standard procedures after cleaning or descumming to produce a photoengraving resist.

The above process, although of great promise, has suffered from the drawback that the boundaries of the relief image are not sharply defined with the result that the reproductions made from them are blurred and unsatisfactory for many purposes. This drawback is due to the fact that the bond between the hardened polymeric image and the base plate is not sufficiently strong with the result that the edges may be undercut by the action of the etchant and/or chipped away by mechanical handling when the recording element is used. Several attempts have been made to solve this problem. For example, anchor coats such as phosphates or chromates have been employed before deposition of the original binder composition. Phosphate anchor coats are obtained by treatment of the metallic surface with phosphoric acid. Chromate anchor coats are formed by treatment of the substrate with a mixture of sulfuric acid and a soluble chromate salt such as sodium dichromate.

It has also been proposed to prepare anchor coats using coordinated compounds of the Werner type. These compounds comprise a well known class of chemicals. They are metallic salts of organic acids which act as catalysts in the oxidation and/or polymerization of drying oils. They include for example, coordination compounds formed by reaction between organic acids and trivalent chromium salts such as the oxychloride. Those Werner compounds which form a film when dried, apparently by thermally induced polymerization and are produced by contact in solution between trivalent chromium salts and aromatic acids such as p-nitrobenzoic acid or saturated or unsaturated aliphatic carboxylic acids containing from three to eighteen carbon atoms are suitable. Unsaturated acids having less than 10 carbon atoms, especially acrylic and methacrylic acids are especially useful. Stearic acid is a widely employed saturated, aliphatic acid. Such compounds are well known and fully described in literature. They are commercially available for example from E. I. du Pont de Nemours & Company of Wilmington, Del., and are sold under the trade names of Volan and Quilon. Volan is described in the literature furnished by the Du Pont Company as a composition of the following type:

	Percent
Methacrylic acid -----	5.1
Chloride -----	8.2
Chromium -----	6.0
Isopropanol -----	40.8
Acetone -----	10.0
Water -----	29.0
Combined oxygen -----	0.9
pH (approximate), 3.4.	

Quilon S is the corresponding stearic acid compound and has a typical analysis as follows:

	Percent
Chrome complex -----	29-30
Isopropanol -----	65-70
Water -----	<5

These Werner compounds or complexes may be used for example, by immersing the metal base in a composi-

tion such as described above and drying before deposition of the binder composition.

These procedures have proved to be unsatisfactory for a number of reasons. Proper application of inorganic anchor coats is so time consuming and requires such careful control that it is difficult to work the anchor coating step into an economical commercial operation. These coatings operate by etching the base metal, and therefore require control of concentration, pH and temperature to insure against over or underetching. Furthermore, the anchor coating must be carefully dried before the binder composition can be applied. This may require as long as four hours at a controlled temperature. The time factor alone is a serious detriment to the commercial preparation of recording elements including inorganic anchor coats such as phosphates or chromates.

In addition, if magnesium is used as a base metal the relief image often chips away in the body of the image and not just at the edges because of the inorganic anchor coats form such a weak bond between this metal and the image.

The Werner complexes are almost totally unsatisfactory on magnesium. On zinc the temperature which is required for drying and the time required for adequate drying is so extended as to be detrimental to the grain structure of the zinc, and results in an imperfect image.

The present invention is therefore directed towards the alleviation of these deficiencies by improving the bonding of the photoconductive binder film to the metal base. To this end a binding or anchoring composition has been devised which not only affords adequate bonding action, but has other highly useful and unexpected benefits, as will be fully apparent hereinafter.

THE INVENTION

It has now been discovered that the deficiencies above mentioned may be overcome by the use of the above-described Werner complexes in compositions containing drying agents. Suitable drying agents include, for example, metallic salts of organic acids suitably naphthenate, octoate, or tallate salts, of cobalt, zinc, lead, manganese, iron and zinc. Such drying agents are used in the proportion of from about 0.5 to about 8% based on the total weight of the Werner compound in aqueous compositions containing the selected Werner compound. The compositions may be provided as concentrates to be diluted so as to contain the described proportions of drying agent.

The concentration of Werner compounds in the aqueous compositions ready for use is from about 0.3% to about 5% based on the total weight of the composition.

The compositions are generally acidic and the pH may be adjusted to obtain optimum results depending upon the selected Werner compound and the base metal. Generally, a pH of from about 3.5 to about 6 is satisfactory although the range may be extended somewhat without detrimental effect.

The compositions of the invention therefore may be broadly described as comprising aqueous compositions containing from about 0.3% to about 5% by weight of a Werner compound together with from about 0.02 to 1.0% by weight of a drying agent at a pH of from about 3.5 to about 6.

The compositions may be applied to the base metal in any convenient manner, for example by spraying, brushing or dipping. It is preferred to dip the metal in the selected composition for from 10 to about 30 seconds. The base metal thus coated is then dried and heated at from 200° F. to about 250° F., preferably 215° F. to 235° F. The time required for treatment is only from about 8 seconds with infrared to about 6 minutes of hardening in the oven.

It will be seen that the use of the compositions of this invention makes possible a process which readily

lends itself to commercial operations. Instead of the high temperatures and long drying periods heretofore required, the whole operation of applying the anchor coat can be completed in less than 1 minute, and at a temperature which is not detrimental to the base metal. Moreover, the bond which is formed between the base and the binder coat is such that the problem of undercutting and chipping away of the relief image whether on its periphery or within the body of the image is substantially alleviated. The compositions may be used with magnesium plates to give wholly satisfactory results. Further, and notwithstanding the higher bonding quality of the anchor coat, it does not interfere with the etching process.

The use of base plates prepared with the compositions of this invention is in accordance with known procedures. The photoconductive film is applied in the usual manner and the recording element thus prepared is utilized in the same way as described above for ordinary recording elements. Photoengraving or lithographic plates may be prepared as may printed circuits or other products of the same class.

An unexpected advantage resulting from the use of the compositions of this invention is that the resist image forms a planar surface which is generally harder than has heretofore been possible. The products therefore will last longer under conditions of ordinary use than lithographic plates made with other treatments of zinc-oxide photoconductive layers. It is believed that in some manner the use of the compositions expedites the diffusion of the polymerization catalyst into the binder composition so that the degree of polymerization of the binder is enhanced.

Preferred Werner compounds for use in this invention contain chromium although others may be used.

The following nonlimiting examples are given by way of illustration only:

Example I.—Preparation of concentrates

Concentrates are prepared by mixing the selected drying agent with the Werner compounds as follows:

(A)		Parts
Volan	-----	98
Cobalt naphthenate	-----	2
(B)		
Volan	-----	80
Quilon S	-----	19
Cobalt naphthenate	-----	1
(C)		
Quilon S	-----	80
Volan	-----	15
Zinc octoate	-----	5

Example II.—Preparation of anchor coat compositions

Anchor coat compositions are prepared as follows:

		Parts
Concentrate A, B or C	-----	3
Water	-----	97
Adjust pH with aqueous ammonia in isopropanol.		
(a) For zinc or aluminum,		
(1) Volan composition	-----	pH 5.5
(2) Quilon S composition	-----	4.5
(b) For magnesium,		
(1) Volan composition	-----	6.0
(2) Quilon S composition	-----	3.5-4.5

Example III.—Preparation of recording element

Recording elements are prepared by immersing zinc, magnesium or aluminum plates in any of the compositions of the second example and holding for from 10 to 30 seconds. The plate is then removed, rinsed, dried with

forced air and heated to 220° F. for 3 minutes. The plates are then coated to a thickness of 0.6 mil (dry) with a mixture containing the following ingredients:

SR-82 (60% solution in xylene)	-----ml--	360
R-830 (60% solution in xylene)	-----ml--	70
Toluene	-----ml--	200
Xylene	-----ml--	600
Zinc oxide	-----g--	520

The recording elements thus prepared are used for the preparation of lithograph and photoengraving plates in accordance with the herein-described procedures.

What is claimed is:

1. A recording element comprising a metallic base having a surface coating comprising an electrically insulating polymeric binder capable of further polymerization under controlled conditions, the said binder having a photo-conductive material dispersed therein, the said film being anchored to the said base by an anchor coat comprising a chromium containing Werner complex which is derived from a carboxylic acid containing from three to eighteen carbon atoms and a drying agent selected from the group consisting of naphthenate, octoate and tallate salts of cobalt, zinc, lead, manganese, iron and calcium.

2. A recording element as in claim 1 wherein the metallic base is selected from the group consisting of zinc, magnesium and aluminum.

3. A recording element comprising a metallic base selected from the group consisting of zinc, magnesium and aluminum having a surface coat comprising an electrically insulating silicone polymeric binder film capable of further polymerization under controlled conditions, the said binder having a photo-conductive zinc oxide dispersed therein, the said film being anchored to the said base with an anchor coat comprising a chromium containing Werner complex which is derived from a carboxylic acid containing from three to eighteen carbon atoms and a drying agent selected from the group consisting of naphthenate, octoate and tallate salts of cobalt, zinc, lead, manganese, iron and calcium.

4. A base plate for use in the production of recording elements comprising a metallic base with a surface coating comprising a chromium containing Werner complex which is derived from a carboxylic acid containing from three to eighteen carbon atoms and a drying agent selected from the group consisting of naphthenate, octoate and tallate salts of cobalt, zinc, lead, manganese, iron and calcium.

5. A base plate as in claim 4 wherein the metallic base is selected from the group consisting of zinc, magnesium and aluminum.

6. In the process of producing a recording element including the step of coating a base metal with an electrically insulating binder film comprising a polymer capable of further controlled polymerization, the said binder having a dispersed photoconductive material dispersed therein, the steps of initially coating the base metal with an aqueous composition having a pH from about 3.5 to 6, and containing from about 0.3% to 5% by weight of a chromium containing Werner complex derived from a carboxylic acid containing from three to eighteen carbon atoms and from about 0.2% to 1% by weight of a drying agent selected from the group consisting of naphthenate, octoate and tallate salts of cobalt, zinc, lead, manganese, iron and calcium, and drying at from about 200° F. to 250° F.

7. A process as in claim 6 wherein the metallic base is selected from the group consisting of zinc, magnesium and aluminum.

8. In the process of producing a recording element including the step of coating a metallic base selected from the group consisting of zinc, magnesium and aluminum with an insulating silicone polymeric binder film capable

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of further polymerization under controlled conditions, the said binder having a photoconductive zinc oxide dispersed therein, the steps of initially coating the base metal with an aqueous composition having a pH from about 3.5 to 6, and containing from about 0.3% to 5% by weight of a chromium containing Werner complex derived from a carboxylic acid containing from three to eighteen carbon atoms and from about 0.2% to 1% by weight of a drying agent selected from the group consisting of naphthenate, octoate and tallate salts of cobalt, zinc, lead, manganese, iron and calcium, and drying at from about 200° F. to 250° F.

9. A process as in claim 7 wherein the metallic base is selected from the group consisting of zinc, magnesium and aluminum.

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GEORGE F. LESMES, Primary Examiner

C. E. VON HORN, Assistant Examiner

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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September 2, 1969

Michael Michalchik

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

Column 2, lines 10 and 11, cancel "the surface of the recording element which accurately reproduces;"; line 57, before "relative" insert -- a charge --.

Signed and sealed this 20th day of January 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents