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## PHOTOENGRAVING RESIST

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## ABSTRACT OF THE DISCLOSURE

This disclosure describes the preparation and use of a recording element in which photoconductive zinc oxide is dispersed in an insulating film composed of an hydroxylated silicone resin and sufficient alkoxy phenyl silane or siloxane so that the alkoxy content of the film is from about 0.3% to about 2% by weight.

This invention relates to 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. The products thus obtained are useful for many purposes.

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, lithography is another. Still another is the production of printed circuits for electrical devices. For convenience and ease of understanding, I will describe my invention 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 an electrostatic printing 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 zinc, magnesium or other etachable metal with a coating composition comprising an electrical insulating film in which a photoconductive material such as zinc oxide is suspended. Photoconductive zinc oxide generally has a surface conductivity of at least about  $10^{-9}$  ohm<sup>-1</sup>/square/watt/cm.<sup>2</sup> when exposed to a wave length of 3900 Å. In most operations, the ratio of zinc oxide to film varies from about 1:1 to about 12:1.

The coating is then made sensitive to light by substantially covering the surface with an electrostatic charge in the dark. One convenient method of charging is exposure of the surface to be charged to a corona discharge produced by connecting one or more fine wires to a direct circuit source, e.g. a direct circuit source of 3–10 kilovolts negative. The atmosphere surrounding the wires is ionized and the ion flow establishes the charge density on the surface. This charge which is usually from 300 to 600 volts, decays slowly in the dark over a period of minutes or hours depending upon the nature of the coating.

The recording element now sensitive to light is exposed by any of the conventional photographic processes and the electrostatic charge is selectively leaked from the surface. The degree of charge decay on a particular area of the charged surface of the recording element is directly proportional to the amount of light to which the area is exposed. If light is projected onto the charged surface through a photoengraving 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

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corresponding areas of the film. There is thus produced a latent electrostatic image on the surface of the recording element which accurately reproduces the negative image on the film.

It is, of course, possible to effect selective charge decay by other procedures. For example, a contact print or a drawing may be focused onto the charged surface of the recording element with the aid of an optical system using light from one or more incandescent lamps.

The insulating film in which the photoconductive material is suspended is a polymeric substance preferably a silicone resin which is capable of further polymerization to produce a polymer of high molecular weight.

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 a mixture of aliphatic hydrocarbons including heptane and homologues thereof. The catalyst particles, by a process which is not completely understood but is probably a triboelectric phenomenon, acquire a positive charge 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 catalyze 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 areas takes place with the result that a polymeric image is produced 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. In the usual case, the image area is resistant to a mixture of aromatic and aliphatic solvents such as a 50:50 combination of heptane or kerosene and xylene or toluene, but the background area is not resistant to said combination. 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 process described above is subject to deficiencies. One of the most important deficiencies is the production of photoengraving resists in which the boundaries of the relief image are not sharply defined. The result is that reproductions which are produced using the resist are blurred and otherwise unsatisfactory for commercial use. Another important deficiency is the inability to achieve reproducible results in ordinary industrial opera-

tions without tedious and extensive quality control procedures. Still another is the expense of the rinsing liquids.

I have found that the basic cause of these deficiencies is the insulating film heretofore employed in the production of recording elements. For example, with the usual films, there is an erratic diffusion of the catalyst with the result that the pattern of polymerization spreads beyond the boundaries of the original electrostatic image with the result that the boundaries of the polymeric image ultimately produced is not sharp and well defined.

The insulating films are usually produced by spraying the insulating base surface with solutions of the partially polymerized insulating film material with zinc oxide or other photoconductive substance suspended therein and then drying to remove the solvent, so as to leave the dry, nontacky, relatively hard, uniform insulator film containing suspended photoconductor.

The silicone film forming materials heretofore employed are extremely sensitive to atmospheric conditions such as relative humidity so that recording elements produced from apparently identical solutions or even from the same solution do not produce identical results. This has necessitated the use of careful control techniques and testing procedures in attempts to insure reproducible results. With recording elements produced using the composition of our invention, these control procedures may be substantially eliminated due to their relative insensitivity to changes in atmospheric conditions.

As stated above, the insulating films of the recording element are preferably silicone resins, i.e. polysiloxanes. These resins as used in the film are partially polymerized and must be capable of further reaction under the influence of the developer catalyst to form high molecular weight solvent resistant polymeric images. For convenience, I shall refer to the relatively low molecular weight polymers of the insulating film as the initial polymer and to the relatively high molecular weight polymer of the polymeric image as the final product.

It is essential that the initial polymer contain functional groups capable of further reaction to produce the final polymer. This has been achieved in the past by utilizing initial polymers with a high hydroxyl group content. During curing, the hydroxyl groups condense to split out water and form oxygen linkages which join the initial polymer molecules together either by chain lengthening or cross-linking or both to form the final polymer. A typical initial polymer widely employed in the production of recording elements is the methyl phenyl polysiloxane mixture available from General Electric Corporation as SR-82. This resin has a high hydroxyl content and is, therefore, capable of undergoing further polymerization to form the final polymer. Other similar initial polymers have been employed.

I have discovered that if instead of using hydroxylated silicone resins as the initial polymer a mixture of hydroxylated silicone resins and alkoxyated siloxanes or silanes is employed, the recording element which is produced is not subject to the disadvantages referred to above. Thus, for example, if the initial polymer comprises a mixture of a hydroxylated siloxane and an alkoxyated siloxane or silane such that the alkoxy content of the mixture on a dry basis is from about 0.3% to about 2% by weight of the total resin, recording elements produced can be used in the preparation of photoengraving plates or resists with sharply defined image boundaries. Moreover, the insulating film on the recording element is remarkably tolerant to changes in atmospheric conditions and the results are reproducible.

I prefer to use lower alkoxyated aryl type silanes and siloxanes such as diphenyl diethoxy silane, or ethoxylated phenyl siloxanes as additives to the initial polymer. These silanes are prepared by esterifying diphenyl dichlorosilane. The siloxanes are prepared by esterifying phenyl chlorosilanes followed by hydrolysis

of the resulting products. Ethyl alcohol may be used as an esterifying agent but alcohols containing up to four carbon atoms may also be used in the preparation of silanes and siloxanes which are useful in our invention.

The products are commercially available from Union Carbide Corporation and others. Diphenyl diethoxy silane is a monomer with a molecular weight of 272. The ethoxylated phenyl siloxanes are polymers with approximate molecular weights of from 500 to 5,000. The alkoxy content, i.e. the average number of alkoxy groups per molecule depends upon the manner of preparation and may vary from 5% by weight or lower to 36% by weight or even higher. It is most convenient to use additives in which the alkoxy content is within this range since these are commercially available, but it is not necessary to do so. Additives in which the alkoxy content is outside of this range may be utilized and the proportion used adjusted so that the alkoxy content of the insulating film varies within the preferred range and from 0.3% to 2% by weight on a dry basis.

The basic concept of my invention is the preparation of recording elements with a photoconductive layer deposited thereon in which the initial polymer of the insulating film comprises a mixture containing a hydroxylated silicone resin and an alkoxy silane or alkoxyated siloxane in which the alkoxy groups contain up to four carbon atoms. The proportions of the ingredients are preferably selected so that the alkoxy content of the insulating film is from about 0.3% to about 2% by weight of the total resin on a dry basis.

The procedures employed utilizing the novel compositions of my invention are the same as with previously known compositions. The metal base plate is cleaned and the surface which is to receive the insulating film is coated with a binder composition such as a phosphate binder or a chromate binder. The binder coating is similar to the coating used whenever a metal is to be coated with plastic as for example, when a metal surface is to be painted. Phosphate binder coatings are obtained by treatment of the surface with phosphoric acid. Chromate coatings are formed by treatment of the surface with a mixture of sulfuric acid and a soluble chromate salt such as sodium dichromate. Binder coatings are not essential to this invention but aid in holding the insulating film to the base.

The insulating film is formed by coating the metal base with a composition comprising a photoconductor such as photoconductive zinc oxide suspended in a solution of the initial polymer mixture. Usually the surface is coated by spraying. The solvent is then removed by evaporation either at room temperature or by heating. The insulating film thus formed is preferably from about 0.4 to 0.8 mil in thickness. Somewhat thinner films will produce useful results but they may not pick up sufficient polymerization catalyst. Film more than 0.8 mil in thickness may be used in some applications, but are generally not desired since the image boundaries of the finished products tend to become less sharp due to diffusion of the polymerization catalyst.

The recording element is used as described above. The electrostatic image is produced and the polymerization catalyst is deposited on the image by immersing the recording element in a developer bath with the catalyst suspended therein and preferably rinsed to remove extraneous catalyst. The recording element is then cured in a curing oven to effect further polymerization of the insulating film in the image area. If aluminum octoates are used as the catalyst, the preferred curing temperature is from about 450° F. to 530° F. and the curing time is from about three to six minutes. The plate with the polymeric image formed thereon is then cooled either by standing at room temperature or quenched in a cooling liquid such as water, and the background removed by washing the plate with a solvent. The plate is then descummed

or cleaned by the usual procedures and it is ready for etching.

A further unexpected advantage of the improved recording elements of our invention is that when rinsing is employed to remove extraneous catalyst, less expensive rinse liquids are necessary. In the past, the rinse liquids utilized have included hydrocarbon solvents mixed with silicone fluids. I have found that in accordance with my invention, excellent results can be achieved with rinse liquids which do not contain any silicone fluids.

While my invention has been specifically described as applied to photoengraving, it can also be used in other application where a recording element is formed by depositing a photoconductive layer on a metal base for the purpose of producing a polymeric image. It can be used, for example in the production of printed copper electrical circuits. For the production of electrical circuits, the recording element comprises a photoconductive layer which is deposited on the copper surface of a copper laminate and an electrostatic image corresponding to the desired circuit formed thereon. The polymer image is formed and the background area dissolved as described above to leave the bare copper. This copper is then removed by etching, for example with ferric chloride or ammonium persulfate solution. The polymer image which covers the circuit is then removed with a solvent such as toluene, to leave bare copper in the desired configuration for the electrical circuit.

#### Example I

A zinc photoengraving plate is cleaned, pumiced and a binder coating is applied. The treated metal is 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 |
| Photoconductive              |     |     |
| zinc oxide                   | g.  | 520 |
| Uranine dye                  |     |     |
| (2% solution in methanol)    | ml. | 6   |

SR-82 is a silicone resin with a high hydroxyl content available from General Electric Company, Pittsfield, Mass.

R-830 is an ethoxylated phenyl siloxane with an ethoxy content of 5% and is available from Union Carbide Corp., New York, N.Y.

The coated plate is dried below 180° F. with air circulation to produce an insulating film with an ethoxy content of 1.4% by weight. The plate is charged, exposed and developed by dipping the plate in an aluminum octoate suspension in a mixture of isooctane, heptane and silicone fluid. The liquid developer is evaporated from the plate and the plate is heated for about four minutes at 500° F. to effect polymerization of the image area of the film. It is then cooled by quenching in water and washed with a 1:1 mixture of xylene and heptane to selectively remove the background portions.

The plate with the polymeric image thereon is rinsed with hot water, blown dry and etched to produce a photoengraving plate.

Similar plates are prepared with other resin mixtures containing hydroxylated silicone resins and sufficient amounts of alkoxyated silanes or alkoxyated siloxanes in which the alkoxy group contains up to four carbon atoms in portions so that the alkoxy content of the insulated film is from about 0.3% to about 2% on a dry basis. The further polymerization of the image area is catalyzed by

aluminum octoate, resinate or other polymerization catalysts.

When recording elements prepared using these mixtures are compared with ordinary recording elements they are found to be much less sensitive to charges in atmospheric conditions. The polymeric images produced from these recording elements have sharp, well defined boundaries compared with those produced from ordinary recording elements.

What is claimed is:

1. In a recording element comprising a photoconductive layer deposited on a metal base, said layer comprising photoconductive zinc oxide suspended in an insulating film formed from a hydroxylated silicone resin, the improvement which comprises the presence in said silicone resin film of a substance selected from the group consisting of alkoxy phenyl silanes and alkoxy phenyl siloxanes, the alkoxy group of said silane and siloxane containing up to four carbon atoms in such amount that the alkoxy content of the film is from about 0.3% to about 2% by weight.

2. A recording element as in claim 1 in which the alkoxy groups are ethoxy groups.

3. A recording element as in claim 1 in which the metallic base is zinc, magnesium or copper.

4. In a process of producing a recording element including the step of forming a photoconductive layer on a metal base, said layer comprising photoconductive zinc oxide suspended in an insulating film formed from a hydroxylated silicone resin, the improvement which comprises the presence in said silicone resin of a substance selected from the group consisting of alkoxy phenyl silanes and alkoxy phenyl siloxanes, the alkoxy group of said silane and siloxane containing up to four carbon atoms in such amount that the alkoxy content of the film is from about 0.3% to about 2% by weight.

5. A process as in claim 4 in which the alkoxy groups are ethoxy groups.

6. A process as in claim 4 in which the metallic base is zinc, magnesium or copper.

7. In a process of producing a polymeric image including the steps of forming an electrostatic image on a recording element, said element comprising a photoconductive layer deposited on a metal base, said layer comprising photoconductive zinc oxide suspended in an insulating film formed from a hydroxylated silicone resin, developing said polymeric image by depositing a polymerization catalyst on said electrostatic image and heating to effect further polymerization of said film, the improvement which comprises the presence in said silicone resin film of a substance selected from the group consisting of alkoxy phenyl silanes and alkoxy phenyl siloxanes, the alkoxy group of said silane and siloxane containing up to four carbon atoms in such amount that the alkoxy content of the film is from about 0.3% to about 2% by weight.

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