

[72] Inventors **Yasuo Ueda**
#3-32, Kitano-cho, Ikuta-ku, Kobe, Hyogo;
Akira Takatsu, #3-5-16, Kusatsu-cho,
Kusatsu, Siga; **Tatsuo Aizawa**, #6-34,
Kuwasu-cho, Higashisumiyoshi-ku, Osaka,
all of Japan
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[31] **41/77666**

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Primary Examiner—George F. Lesmes
Assistant Examiner—John C. Cooper, III
Attorney—Milford A. Juten

[54] **ZINC OXIDE BINDER PLATE FOR CHARGELESS ELECTROPHOTOGRAPHY**
2 Claims, 4 Drawing Figs.

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96/1, 252/501
[51] Int. Cl..... **G03g 13/22,**
G03g 5/08
[50] Field of Search..... **96/1.8, 1.5**
252/501

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ABSTRACT: An electrophotographic plate for chargeless electrostatic printing and the method of making the same using a photoconductive material such as microcrystalline zinc oxide and a binder of suitable type with an organic acid such as citric, oxalic or malic and mixing the ingredients and applying them to a baseplate in the desired proportions to control the sensitivity of the electrophotographic plate to light and to control the recovery of memory effect so that the electrophotographic plate can be subject to ordinary light and still be usable for reproduction by being placed in the dark for a short period of time so that the recovery of the memory effect takes place and the electrophotographic plate can then be used for reproduction thereby greatly simplifying the storage of the electrophotographic plates and also greatly simplifying the manufacture thereof. The electrophotographic plate having a smooth glossy surface thereby preventing adherence of the toner to the nonimage areas.

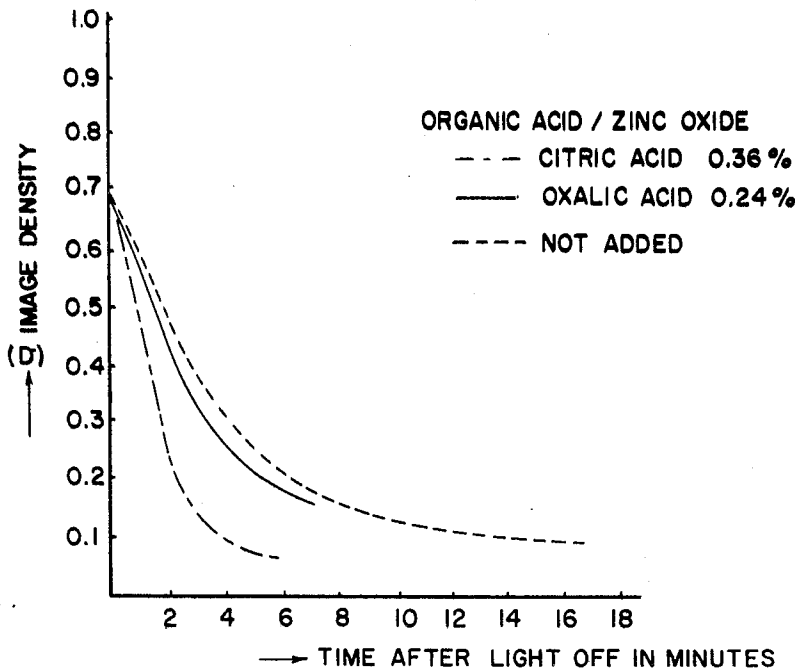


FIG. 1

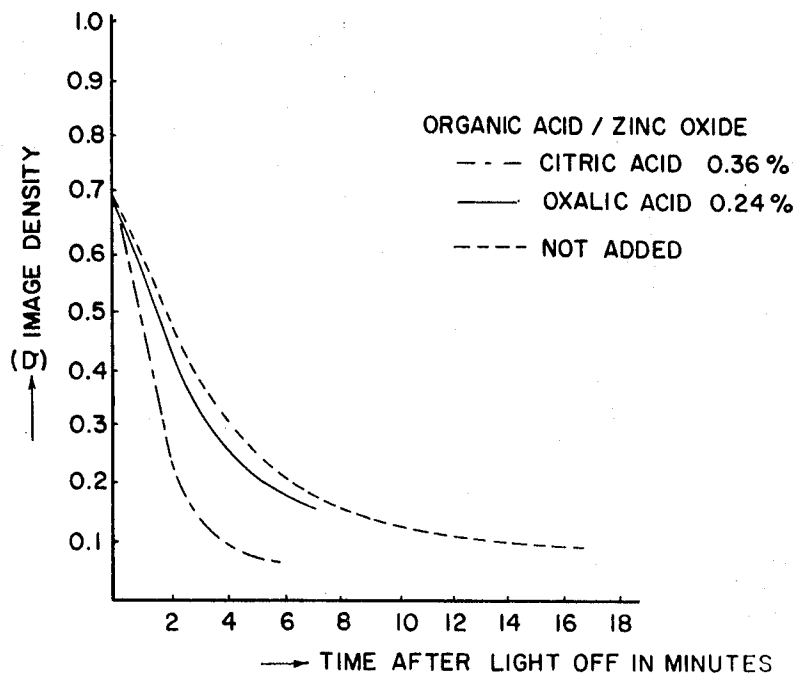
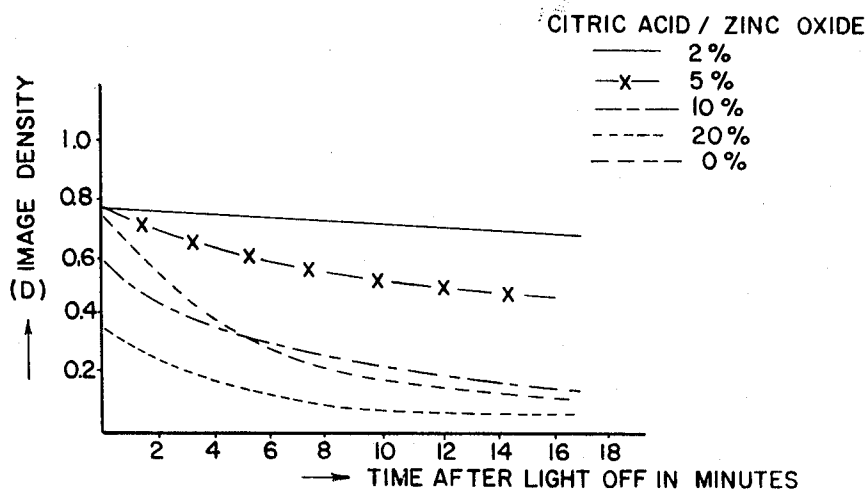


FIG. 2

INVENTOR.
YASUO UEDO
AKIRA TAKATSU
TATSUO AIZAWA

BY

Milford A. Jerten
Attorney

FIG. 3

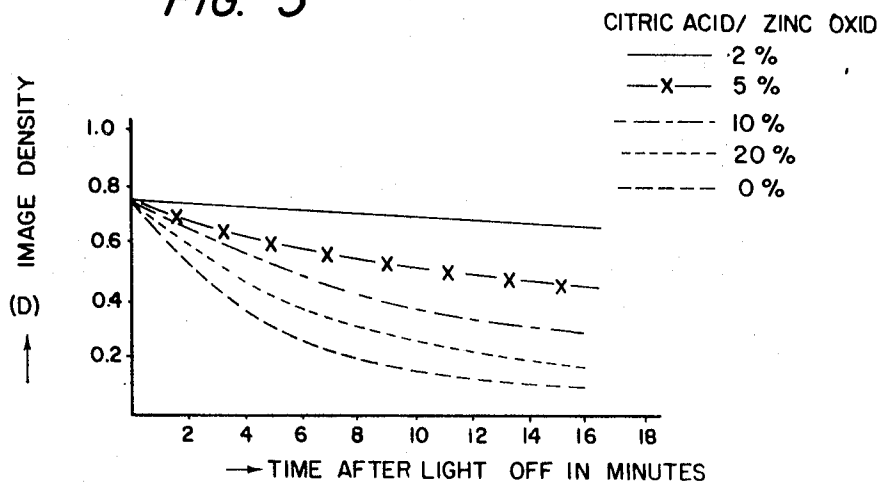
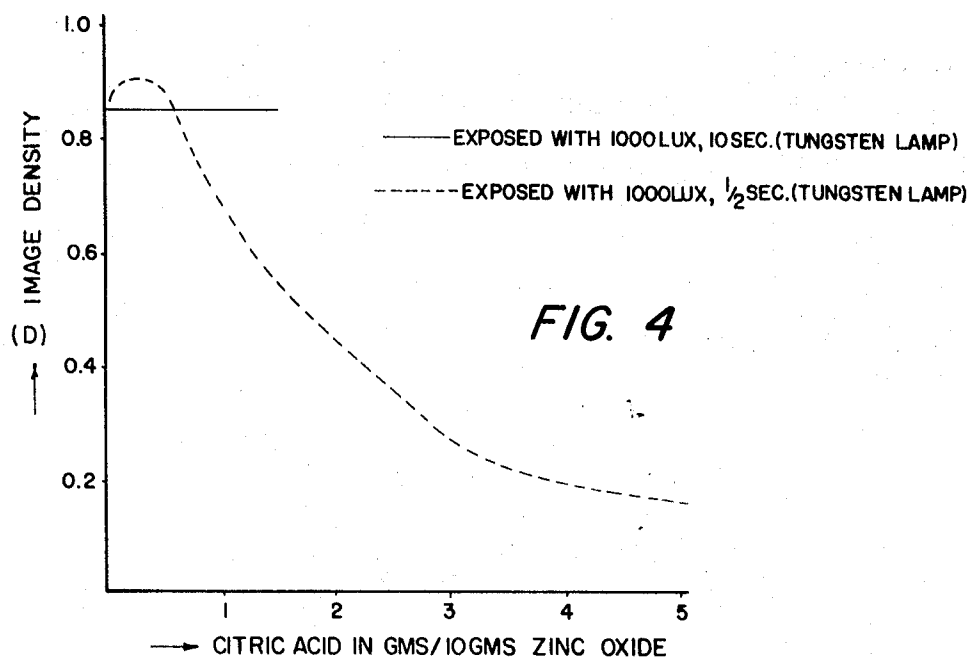


FIG. 4

INVENTORS
YASUO UEDO
AKIRA TAKATSU
TATSUO AIZAWA

By
Trifford A. Julien
attorney

ZINC OXIDE BINDER PLATE FOR CHARGELESS ELECTROPHOTOGRAPHY

This invention relates to chargeless electrostatic printing and particularly to a method of producing an electrophotographic plate for use in the chargeless electrostatic-printing process.

The electrophotographic plate of this invention is made by a process whereby the time required for recovery of the memory effect can be controlled to obtain the desired characteristics, particularly with respect to the irradiation effect caused by exposing the electrophotographic plate to light.

Heretofore in the chargeless electrostatic-printing processes electrophotographic plates have been prepared by mixing a photoconductive material of the N type such as zinc oxide and a resin binder and coating a baseplate with the resulting mixture and drying the coating. The photoconductive coating layer of such an electrophotographic plate is kept in the dark and while in the dark is exposed to a light image to be recorded so that the "Dember effect" takes place, i.e. electrons are removed into the body of photoconductive coating layer and positive holes are trapped near the surface of the photoconductive coating layer. Thus, the electrical double layer is formed in the photoconductive coating layer and then an electrically charged toner is applied to the exposed photoconductive coating layer to form a visible image. It will be apparent that the images fixed by any of the usual means such as heat or the like.

This prior art process has a number of disadvantages: (1) an image of satisfactory contrast is not obtained; (2) the time required for developing is too long; (3) the fog produced in the nonimage or the background areas is excessive; (4) it is not possible to promptly use the electrophotographic plate after the electrophotographic plate has been exposed to light.

A principal object of this invention is to provide a method of making an electrophotographic plate and the product thereof which overcomes the above-described difficulties and produce an electrophotographic plate for use in the chargeless electrostatic printing process.

Another object is to control the time required for recovery of the memory effect by adding organic acid to a photoconductive material and a binder.

A further object is to provide a process whereby the sensitivity of an electrophotographic plate can be diminished by adding organic acid to a photoconductive material and a binder.

A still further object is to produce an electrophotographic plate using both water-soluble resins and organic solvent resins as binders.

A further object of this invention is to produce a satisfactory dispersion of the ingredients of an electrophotographic coating layer and shorten the milling time by adding an organic acid to the photoconductive material and a binder.

A still further object is to produce a smooth photoconductive coating layer by including an organic acid with a photoconductive material and a binder.

Other and further objects will be apparent as the description proceeds and upon reference to the accompanying drawings wherein:

FIG. 1 is a graph showing decay curves of the time required for recovery of the memory effect showing the relation between the density of the developed image at various times after the exposure light is turned off, showing the comparison of electrophotographic plates with organic acid added with respect to an electrophotographic plate without organic acid.

FIG. 2 is a graph showing the decay curves of the time required for the recovery of the memory effect showing the relation of the density of the developed image and the concentration of citric acid included in the coating layer of an electrophotographic plate, the exposure being 5 seconds at 1,000 lux intensity.

FIG. 3 is a graph showing the decay curves of the time required for the recovery of the memory effect showing the relation of the density of the developed image with respect to

the citric acid concentration in the electroconductive coating on the electrophotographic plate, the exposure to light being 10 seconds at 1,000 LUX which is the saturation exposure to light.

FIG. 4 is a graph illustrating how the sensitivity of the electrophotographic plate diminishes as the citric acid concentration is increased with respect to the photoconductive material.

Now, in accordance with this invention it has been found that the memory effect is controlled by adding organic acids having carboxyl groups such as oxalic acid, citric acid and malic acid to microcrystalline photoconductive material such as zinc oxide and with water soluble resins such as polyvinyl acetate emulsion or polyvinyl acetal or both polyvinyl acetate emulsion and polyvinyl acetal which have a lower resistance than the photoconductive material.

From FIGS. 1 and 3 it will be evident that recovery from the memory effect is rapid when less than 100 mg. of citric acid per 10 g. of zinc oxide is included in the electrophotographic coating layer. These figures also illustrate that it is possible to cause the memory effect to last for a longer time by adding more than 100 mg. of citric acid per 10 g. of zinc oxide. However, as the citric acid concentration is increased further, the developed image becomes indistinct and the background areas and the image areas become hardly distinguishable from one another.

Upon reference to FIGS. 2 and 3 it will be noted the sensitivity of the photoconductive coating layer diminishes as the organic acid concentration is increased. The organic acid therefore serves as a desensitizer as the organic acid concentration is increased. This relation appears obvious when adding citric acid and the following effects are also found:

1. The photoconductive coating layer becomes smooth and prevents toners from adhering to the nonimage areas and therefore there is a minimum of fog in the background or nonimage areas.

2. The milling time for mixing the ingredients of the coating can be made very short, thereby reducing the time and the expense of manufacture.

3. The ingredients of photoconductive coating when they are mixed together cause the "Thixotropy effect" to take place thereby producing a coating which can be effective and uniformly applied to the baseplate material such as art paper, polyethylene film or the like.

From the results that the mixture of adding citric acid to zinc oxide is neutral it is believed that a reaction product between the zinc oxide and the citric acid solution takes place.

Water-soluble resin is employed as a binder in the above description.

However, organic solvent resin may be added to the crystallization product of the reaction of the zinc oxide with the organic acid such as citric acid.

The following examples illustrate the invention and it is to be understood that such examples are for the purpose of facilitating the practice of the invention and not by way of unnecessary limitation.

EXAMPLE I

Microcrystalline zinc oxide (the grain size between 0.1 μ and 0.3 μ)	100 g.
0.12% solution of citric acid	300 cc.
Polyvinyl acetate emulsion (purity 100%)	20 g.
Polyvinyl alcohol (polymerization degree 550)	15 g.

The above ingredients are milled for about 30 minutes and the mixture is coated to 15 μ thickness on art paper and is dried. The electrophotographic plate thus produced is closely exposed to incandescent light of 1,000 lux for 2 to 3 seconds, thereby an electrostatic latent image is produced thereon, which image is thereafter developed by immersing for 10 seconds in a negatively charged liquid developer to form a visible image.

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The developed image can be chosen to be negative or positive with respect to the original according to whether the charging of the developed is negative or positive.

Citric acid prevents vinyl acetate emulsion from gelling and the electrophotographic plate has a glossy and smooth photoconductive coating layer. The electrophotographic plate recovers from the memory effect within only 3 minutes, so that it is easy to treat in the light.

EXAMPLE II

Microcrystalline zinc oxide (the grain size between 0.1 μ and 0.3 μ)	100 g.
1.5% solution of citric acid	300 cc.
Polyvinyl acetate emulsion (purity 100%)	20 g.
Polyvinyl acetal (purity 100%)	15 g.

The above ingredients are milled for about 30 minutes and the mixture is coated to 15 μ thickness on art paper and is dried. Further processing is performed as indicated in Example I.

The electrophotographic plate according to Example II has the same glossy and smooth photoconductive coating layer as in Example I.)

The electrophotographic plate of Example II requires more time for the recovery of the memory effect than that of Example I.

EXAMPLE III

Microcrystalline zinc oxide (the grain size between 0.1 μ and 0.3 μ)	100 g.
0.12% solution of citric acid	300 cc.
Polyvinyl acetate emulsion (purity 100%)	20 g.
Polyvinyl acetal (purity 100%)	15 g.

The above ingredients are milled for about 30 minutes and the mixture is coated to 15 μ thickness on art paper and is dried. Further processing is performed as indicated in Example I.

The electrophotographic plate according to Example III has the same glossy and smooth photoconductive coating layer as in Examples I and II.

The electrophotographic plate of Example III recovers from the memory effect within only 3 minutes as in Example I.

EXAMPLE IV

Microcrystalline zinc oxide (the grain size between 0.1 μ and 0.3 μ)	100 g.
0.06% solution is oxalic acid	300 cc.
Polyvinyl acetate emulsion (purity 100%) 20 g.	
Polyvinyl acetal (purity 100%)	15 g.

The above ingredients are milled for about 30 minutes and the mixture is coated to 15 μ thickness on a polyethylene film and is dried. Further processing is performed as indicated in Example I.

The electrophotographic plate according to Example IV has the same glossy and smooth photoconductive coating layer as Examples I, II and III.

The electrophotographic plate of Example IV recovers from

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the memory effect more quickly than the case of adding no organic acid.

All said Examples have also the advantages that the exposing and milling times are very short, and the developed image is obtained with clarity and definition, moreover, fog is almost entirely avoided in the background areas.

From the above description it will be evident that the present invention has numerous advantages over the prior art by the addition of the organic acid in a limited amount it has been possible to produce an electrophotographic plate which can recover from the memory effect within only 3 minutes so that the electrophotographic plate can be subject to ambient light up until just a very short time before it is desired to make a reproduction. The electrophotographic plate can then be placed in the dark for the 3 minute period to recover from the memory effect and a good image can be made by exposure to light thereby producing a latent image and developing such latent image promptly.

It is also possible to control the length of time required for the recovery from the memory effect and to decrease the sensitivity of the electrophotographic plate by increasing the amount of the organic acid and therefore when the sensitivity is decreased and the memory effect is increased the electrophotographic plate does not have to be developed immediately after exposure and therefore the present invention has a substantial advantage over prior art electrophotographic plates which have to be developed immediately after exposure.

Another advantage of the invention results in the reduction of the milling time required to mix the ingredients since the presence of the organic acid with the zinc oxide makes it possible to reduce the milling time required thereby producing a substantial advantage over the prior art methods.

It will be apparent that changes may be made within the spirit of the invention as defined by the valid scope of the claims.

1. An electrophotographic plate for chargeless electrostatic printing, comprising a base and a photoconductive layer coated thereon, wherein said photoconductive layer consists essentially of a photoconductive zinc oxide treated with an organic acid selected from the group consisting of oxalic acid, citric acid and malic acid and dispersed in a water-soluble binding material, said binding material being selected from the group consisting of (a) a blend of polyvinyl acetate with polyvinyl alcohol and (b) a blend of polyvinyl acetate with polyvinyl acetal whereby a rapid and controlled recovery from exposure to ambient light is obtained, the organic acid being present in an amount between 0.36 and 20 percent of the photoconductive zinc oxide.

2. A method of chargeless electrostatic printing, which comprises forming a light image on an electrophotographic plate without charging it before hand, thereby producing an electrostatic image on the said plate and developing the said plate with a toner having electrical charges, characterized in that said electrophotographic plate comprises a base and a photoconductive layer coated thereon, said photoconductive layer consisting essentially of a photoconductive zinc oxide treated with an organic acid selected from the group consisting of oxalic acid, citric acid and malic acid and dispersed in a binding water-soluble material selected from the group consisting of (a) a blend of polyvinyl acetate with polyvinyl alcohol and (b) a blend of polyvinyl acetate with polyvinyl acetal whereby a rapid recovery from exposure to ambient light is obtained, the organic acid being present in an amount 0.36 and 20 percent of the photoconductive zinc oxide.