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Yoskida

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[54] **METHOD OF FORMING COLORED COPY OF AN ORIGINAL**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** ..... **117/17.5,** 96/1 R, 96/1 SD, 96/1.2, 117/36.2, 117/36.8, 355/4

[51] **Int. Cl.** **G03g 13/08**

[58] **Field of Search** ..... 117/17.5, 36.2, 36.8; 96/1 R, 1 SD, 1.2; 355/3, 17, 4

[56] **References Cited**

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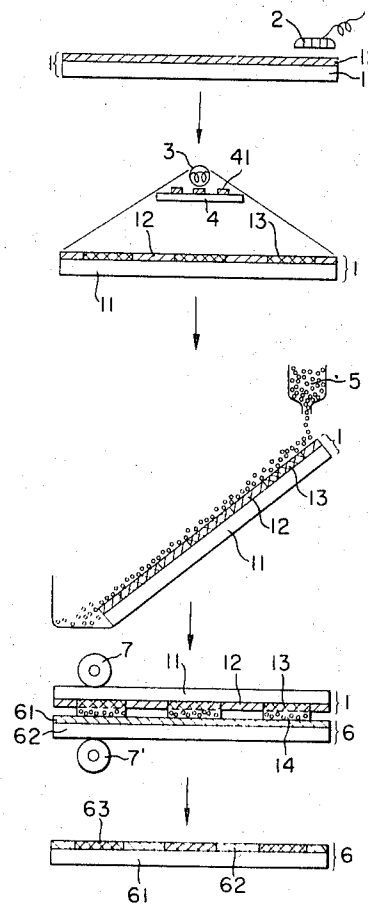
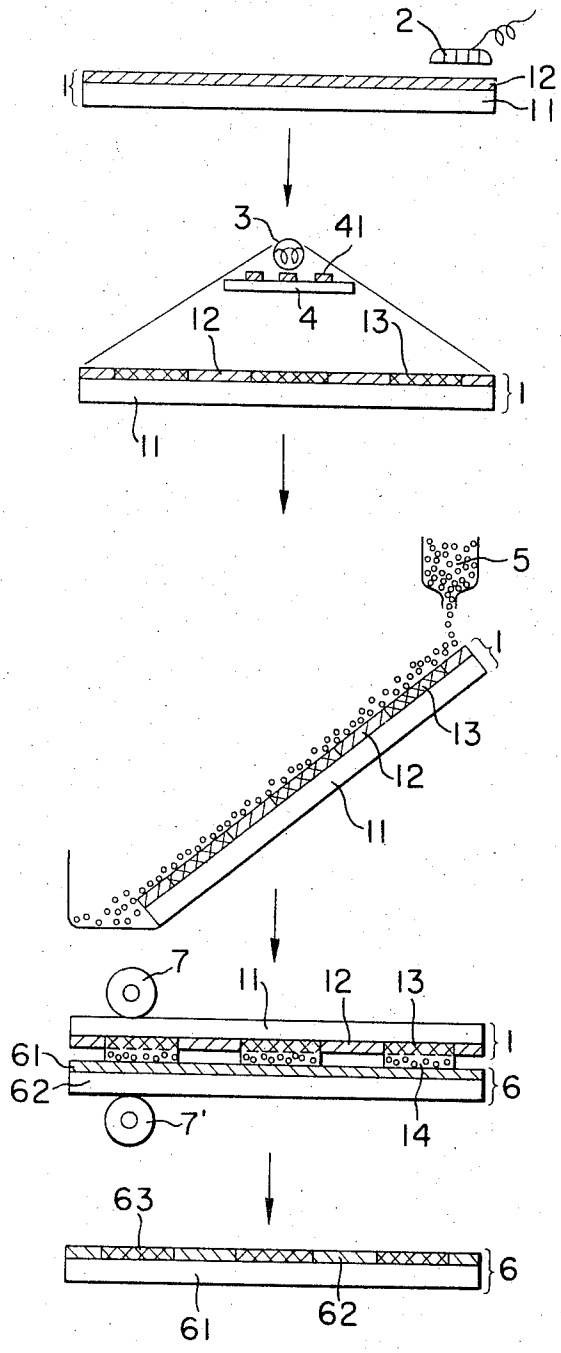
Attorney, Agent, or Firm—Cooper, Dunham, Clark, Griffin & Moran

[57] **ABSTRACT**

A copying method comprising the steps: spreading a fine silica or alumina powder having absorbed thereon a reactive substance A, which can form a colored substance by heating in contact with a reactive substance B, on the surface of a photoconductive layer having an electrostatic latent image thereon; bringing the thus treated surface of the photoconductive layer into contact with the surface of a sheet coated with a reactive substance B and heating to form a colored reaction product on the surface of the sheet replicating the electrostatic image.

6 Claims, 1 Drawing Figure

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METHOD OF FORMING COLORED COPY OF AN ORIGINAL

BACKGROUND OF THE INVENTION

The present invention relates to a method of obtaining copies continuously by utilizing combined electrostatic photography and chemical photography.

The diazo copying method is presently widely used because of its advantages with respect to cost and superior quality of the colored image. When compared with the silver salt method or electrostatic photography, however, it is inferior in photosensitivity. As a result it is not possible to produce copies from a duplex print or an opaque single-side print.

Electrostatic photography is widely employed as a means for producing copies from a duplex print. The method comprises the steps of imparting an electrostatic latent image onto a photoconductive layer of a sensitive material on a support sheet such as paper, metal and the like by electrically charging and selectively leaking the charge by exposure to direct or reflected light from an original to produce a latent image; causing toner particles charged with electricity having the polarity opposite to that of said latent image to adhere to the latent image to form a toner image; and fixing the toner image. This method, however, is defective in that the photoconductive material is expensive and the toner — which is a coloring matter in itself — leaves stains wherever it is scattered. In the case of wet-development, there are various problems arising from incomplete elimination of the solvent from the copies. In the case of dry-development, a high temperature heater is required to fix the image.

SUMMARY OF THE INVENTION

The present invention provides a simple and economical copying method which is capable of substantially alleviating the foregoing defects of the conventional methods and is particularly suited for the purpose of obtaining copies continuously.

The present invention comprises the steps of:

1. Depositing on a latent electrostatic image formed in a photoconductive substrate a particle image comprising fine particles of silica or alumina having adsorbed thereon at least one first member of a color forming set of chemical compounds;
2. Bringing the thus formed particle image into face to face contact with the coated surface of a carrier sheet, said coating comprising at least one second member of the color forming set; and
3. Heating to a temperature which during the period of contact and heating is not destructive of the photoconductive substrate or the carrier sheet; said color forming set comprising at least two chemical compounds which will react with each other to form a colored product during the heating period.

Normally the color forming set will include only two chemicals, although three or more may be involved. One or more may be on the fine particles or on the carrier sheet. For convenience the compound or compounds on the particles will hereinafter be referred to as reactive substance A, and the compound or compounds on the carrier sheet as reactive substance B.

The photoconductive substrate may be any of those substrates presently employed in the art. The carrier sheet may be paper, polymer, metallic foil and the like.

Reactive substance A reacts with reactive substance B to produce a colored product duplicating the original. It appears that reaction takes place by melting or fusing the substances in contact with each other or by sublimation.

A feature of the present invention is the discovery that fine particles of porous silica or alumina can be deposited on a latent image and will adhere thereto whether the electric charge of the latent image is positive or negative. When the fine particles of silica or alumina with reactive substance A adsorbed thereon are brought into contact with an electrostatic latent image charged with positive or negative electricity, the particles are deposited electrostatically on the latent image and will adhere thereto. Next, when this latent image with said particles adhering thereto is brought into pressure contact with a copying or carrier sheet coated with reactive substance B and heated while in such contact, suitably with a roller having a surface temperature of from about 50° to 120°C, the reactive substance A shifts onto said copying sheet to give rise to a reaction in the contact region, whereby a copied color image can be formed. A particular advantage of the process is that the copied image thus obtained, because of its having been formed by reaction between reactive substance A and reactive substance B, does not take the form of an embossed image rising on a flat surface like the toner image to be formed in the electrostatic photography.

The accompanying drawing is a diagrammatic representation of one embodiment of the present invention, wherein: **1** denotes a sensitive material for use in electrostatic photography provided with the photoconductive layer **12**, **2** denotes a corona discharger, **3** denotes a light source, **4** denotes a microfilm carrying an image **41**, **5** denotes a fine powder of silica or alumina having adsorbed thereon a reactive substance A, **13** denotes an electrostatic latent image, **6** denotes a copying sheet provided with a layer **62** containing a reactive substance B, **14** denotes a toner-adhering image, and **63** denotes a copied image.

To be more detailed, the numeral reference **1** denotes a sensitive material for use in electrostatic photography comprising a support **11** and a photoconductive layer **12**, **2** denotes a corona discharger, **3** denotes a light source, **4** denotes a microfilm carrying an image **41**, **5** denotes a fine powder of silica or alumina with adsorbed reactive substance A, **13** denotes an electrostatic latent image, **6** denotes a copying sheet comprising a support **61** and a layer **62** comprising the reactive substance B, **14** denotes a toner-adhering image resulting from the adhesion of the fine powder to the latent image **13**, **7** and **7'** denote rollers for the purpose of bringing the sensitive material **1** into contact with the copying sheet **6** with the application of pressure, and **63** denotes a copied image. Roller **7'** is heated to the selected temperature. First the photoconductive layer side **12** of the sensitive material **1** for use in electrostatic photography is charged by means of the corona discharger **2**. When this charged surface is exposed to the projector's light source **4** through the positive film **4** (in this case a duplex printing original is employed, the reflection light thereof is applied), an electrostatic latent image **13** is formed on the charged surface which corresponds to the image **4** of the original. Next, when

the fine powder of silica or alumina **5** with adsorbed reactive substance A is spread on the surface utilizing, for instance, the cascade method. The powder forms a toner image **14** on the latent image-carrying surface regardless of the polarity of the electrostatic latent image. And then, when the surface of sensitive material **1** which carries the toner image **14** is contacted with the layer **62** containing the reactive substance B under pressure by passage between the rollers **7–7'** as shown, reactive substance A melts or sublimates and transfers to copying sheet **6,** whereon it reacts with the reactive substance B in the contact area and forms the copied color image **63.** The roller **7** is provided with a heater of standard design not shown in the drawings. The sensitive material having the toner image **14** on its photoconductive layer **12** can serve repeatedly as a transfer master until reactive substance A becomes exhausted. This is a particular advantage of this invention which makes possible the production of multiple images in a continuous manner from one master sheet. Additionally, the used sensitive material may be reused after wiping with a revolving brush or the like and applying infrared rays to cure the fatigue condition which arises from exposure of the photoconductive layer. This too is an important advantage of the invention since the same photoconductive substrate can be used repeatedly for copying. The advantages markedly reduce the cost of producing copied images particularly when compared to the photoconductive zinc oxide process.

In order to practice the method of the present invention continuously, it is convenient to repeat the foregoing processes by employing, for instance, an endless belt-type sensitive material such as a selenium drum.

The fine powders of silica or alumina with adsorbed reactive substance A for use in the present invention are different from the conventional toner particles to be made to adhere to electrostatic latent images electrically. They are further characterized in that they do not give rise to the so-called edging effect which is a serious problem in electrostatic photography. Accordingly, it can produce images having a continuously gradated concentration in proportion to the charged electricity.

The fine powder of silica or alumina utilized in the present invention typically will have a grain size of from about 0.1 to 500 μ — preferably 1 to 200 μ — in order to obtain optimum effects. With grain size appreciably smaller, the particles tend to adhere to non-image areas resulting in a stained background at the time of transfer to a copying sheet.

Reactive substance A adsorbed to the silica or alumina, and reactive substance B to be coated on the copying sheet include, for example, the compounds listed below:

Reactive substance A	Reactive substance B	Developing color
(a) Crystal violet lactone	(m) attapulgite clay	blue
(b) dianisidine base	do. do.	light brown
(c) 4-nitro-O-anisidine	do. do.	yellow
(d) Rhodamine lactone	do. do.	red
(e) gallic acid	(m) ammonium methavanadate	black
(f) monoethanol amine	(o) copper sulfate	dark blue
(g) 2,3-dihydroxy naphthalene	(p) 2-diazo-4-chloro-1-phenol	light brown
(h) 8-amino-1-naphthol-5,7,-disulfonic acid	do. do. do.	violet
2,3-dihydroxy naphthalene	(q) 4-diazo dipropyl aniline	blue
do. do. do.	(r) 4-diazo ethylbenzyl aniline	blue
(i) 4-methoxy-1-naphthol	4-diazo dipropyl aniline	blue
(j) 1-phenyl-3-carboxy pyrazolone	do. do. do.	red
do. do. do.	4-diazo ethylbenzyl aniline	red
(k) phloroglucinol	4-diazo propyl aniline	black
(l) 3-hydroxy-1-phenol	4-diazo ethylbenzyl aniline	yellow

This list, of course, is not limiting, but merely exemplary.

For the preparation of the copying sheet, a solution of the reactive substance B — or this solution mixed with some resinous binder and/or stabilizer and other additives as occasion demands — is applied to a suitable support in a conventional manner.

It should be pointed out that if substance B is such a one as can be melted or sublimated by heating, it may be employed as the reative substance A to be adsorbed to silica or alumina. In other words the substance may be interchangeable. For instance, in the case of combining (g) with (p) or (h) with (p) in the foregoing table, (p) can serve as the reactive substance A, and (g) and (h) serve as the reactive substance B respectively.

The reactive substance A is substantially non-volatile as long as it is adsorbed to the fine powder of silica or alumina, so that even a prolonged storage will not deprive it of its desired effect. The ratio of the fine powder of silica or alumina to the reactive substance A to be applied may vary within wide limits depending for example, on the grain size of silica or alumina, the molecular weight and transferability of the reactive substance B, etc. Normally it will be from about 1 to 10 percent by weight of the reactive substance A based on 10 percent by weight of the fine powder of silica or alumina.

The photoconductive member for use in electrostatic photography to be employed in the present invention

can be provided by applying photoconductors such as zinc oxide, titanium oxide, cadmium oxide, selenium, polymer of N-vinyl carbazole, in a suitable binder to a substrate in the usual manner.

The following non-limiting examples are given by way of illustration only.

EXAMPLE 1

silicone resin liquid (solid matter: 60%) (under the trade name of KR-211, manufactured by Shinetsu Kagaku K.K.)	100g
toluene	100g
zinc oxide powder	80g
Rose Bengale (0.1%)	10cc

The above mixture was made into a coating liquid for use in forming a photoconductive layer through 24 hours' kneading and pulverization in a ball-mill. This coating liquid was then uniformly spread over an aluminum foil so as to obtain a coating film 20 μ thick when dried, whereby a sensitive plate for use in electrostatic photography was prepared. After charging this sensitive plate with negative electricity by corona discharger, a latent image was formed on the electrified surface of said sensitive plate through 3 seconds' irradiation onto a 35 mm positive film disposed at a distance of 40 cm therefrom under the lamp of an enlarger equipped with a 100 W tungsten lamp and a lens of F 2.8 and 6 cmϕ.

Meanwhile, a white, dry fine powder of silica adsorbed Crystal Violet lactone was prepared by thoroughly mixing 40 g of a fine silica powder having a mean grain size of 40 (a manufacture of SHIONOGI SEIYAKU K.K.; trade name: CARPLEX) with 10 g of diphenyl chloride solution containing 1 percent of Crystal Violet lactone. Next, the thus obtained powder was sprinkled on the latent image-carrying surface of said sensitive plate by cascade method, whereby a transfer master was prepared. On the other hand, another coating liquid according to the following prescription was prepared, and by applying this liquid to a white stencil paper weighing 60g/m^2 and drying thereafter, a copying sheet was prepared.

water	1 liter
attapulgite clay (a manufacture of FUJI-DAVIDSON K.K.; trade name: Silloid 244)	40g
polyvinyl acetate emulsion (a manufacture of SS-ZN KOBUNSHI KAGAKU K.K.)	80g

When the surface of this copying sheet was fixed under pressure to the Crystal Violet lactone-adhering surface of the foregoing master by applying heat onto the side of master sheet by means of an iron having a surface temperature of 70°C, a positive dark-blue image was formed on the copying sheet. In this connection, said master showed no deterioration of its photoconductive layer even after producing more than 100 copies of excellent quality continuously.

EXAMPLE 2

benzene	150cc
poly-N-vinyl carbazole (a manufacture of BASF Co., West Germany; trade name: Rubican M-170)	6g
Rhodamine B (a manufacture of TOKYO KASEI K.K.)	0.3g

A coating liquid for use in forming a photoconductive layer according to the above prescription was applied to a tracing paper weighing 75g/m^2, whereby a sensitive paper for use in electrostatic photography was obtained. Subsequently, latent image was formed on this sensitive paper by imparting negative electricity and exposing. Meanwhile, a white, dry fine powder of silica adsorbed 2,3-dihydroxy naphthalene was prepared by thoroughly mixing **10**g of a fine silica powder having a mean grain size of 5μ (a manufacture of FUJI-DAVIDSON K.K.; trade name: Silloid 79) with 10g of a solution containing 100cc of water, 20cc of ethylene glycol and 10g of 2,3-dihydroxy naphthalene. Next, the thus obtained powder was sprinkled over the foregoing latent image by cascade method, whereby a transfer master was prepared. On the other hand, another coating liquid according to the following prescription was prepared, and by applying this liquid to a white stencil paper weighing 60g/m^2 and drying thereafter, a copying sheet was prepared.

water	1 liter
citric acid	10g
aluminum sulfate	15g
4-diazo dipropyl aniline· 1/2 $ZnCl_2$	20g
Patent Pure Blue	0.1g
saponin	1g

When the surface of this copying sheet was fixed to the surface of the foregoing master sheet by heating and lightly pressing with a roller having a surface temperature of 60°~80°C from the back of said master sheet (i.e., the support side), a very sharp, highly concentrated blue image was formed on the surface of the photosensitive layer. As this copy still had the remnant of diazo compound on its non-image area and assumed a yellow color, it was exposed to a high-tension mercury-arc lamp, thereby obtaining a copy having white background. The foregoing master sheet can serve until its reactive substance gets exhausted, but, in the present example, it was possible to produce as many as five copies successively.

EXAMPLE 3

amorphous selenium powder	100g
ethyl cellulose (a manufacture of KOKUSAN KAGAKU K.K.)	30g
dioctyl phosphate (plasticizer)	5g
ethyl acetate	300g
toluene	50g

A mixture according to the above prescription was made into a coating liquid for use in forming a photoconductive layer through 24 hours' kneading and pulverization by means of a ball-mill. This coating liquid was then spread over an aluminum foil so as to obtain a coating film of 30 μ thick when dried, whereby a sensitive plate for use in electrostatic photography was prepared. When this sensitive plate was treated in the same way as in Example 1 except for charging it with positive electricity, there was obtained an excellent copy like the preceeding examples wherein the charged electricity was negative.

EXAMPLE 4

Three varieties of powder developers were prepared as follow:

Developer A (for use in cyan-coloring)	
fine alumina powder having a mean grain of 10 μ (a manufacture of MIZUSAWA KAGAKU K.K.; trade name: NEOBEAD)	10g
water	5g
ethylene glycol	5g
2,3-dihydroxy naphthalene	5g
Developer B (for use in yellow-coloring)	
fine alumina powder having a mean grain size of 10 μ (a manufacture of MIZUSAWA KAGAKU K.K.; trade name: NEOBEAD)	10g
water	5g
ethylene glycol	5g
3-hydroxy-1-phenol	3g
Developer C (for use in magenta-coloring)	
fine alumina powder having a mean grain size of 10 μ (a manufacture of MIZUSAWA KAGAKU K.K.; trade name: NEOBEAD)	10g
water	5g
ethylene glycol	5g
1-phenyl-3-carboxy pyrazolone	3g

On the other hand, a sensitive plate for use in electrostatic photography was prepared in the same way as in Example 1. After charging this sensitive plate with negative electricity by corona discharger, a latent image was formed on the electrified surface of said sensitive plate through about 5 seconds' irradiation onto a 35 mm positive color film along with a red filter which were disposed at a distance of 40cm therefrom under the lamp of an enlarger equipped with a 100W tungsten lamp and a lens of F 2.8 and 6cm ϕ. Subsequently, said developer A was sprinkled on the latent image-carrying sensitive plate to be adsorbed thereon, whereby a master for use in cyan-coloring was prepared. Meanwhile, a coating liquid prepared according to the following prescription was applied to a white stencil paper weighing 60g/m^2 and dried thereafter, whereby a copying sheet was prepared.

water	1 liter
tartaric acid	5g
4-diazo ethylbenzyl aniline· ½ $ZnCl_2$	35g
saponin	1g

When the surface of this copying sheet was pressed against the surface of the foregoing master and heated by a heating roller having s surface temperature of 70°C onto the mastersheet side, a cyan-colored image was formed on the copying sheet. Subsequently, when the same copying sheet was treated in the same manner as above by applying the developer B in the case of the blue filter and the developer C in the case of the green filter, there was obtained a copied image of color. On this occasion, a part of the image area and the non-image area assume a yellow color due to some unreacted diazo compound. However, it is possible to render a white backround, if necessary, through overall exposure to a fluorescent lamp.

EXAMPLE 5

In Example 1, by substituting 1 percent aqueous solution of gallic acid for diphenyl chloride solution containing 1 percent of Crystal Violet lactone and employing 3 percent aqueous solution of ammonium methavanadate as the coating liquid for copying sheet, a clear-cut black-colored image was obtained.

What is claimed is:

1. A copying method comprising the steps of:

1. Depositing on a latent electrostatic image carried on a photoconductive substrate a particle image comprising fine porous particles of silica or alumina having a mean grain size from about 0.1 to 500, and having adsorbed thereon at least one first member of a color forming set of chemical compounds;
2. Bringing the thus formed particle image into face to face contact with the coated surface of a carrier sheet, said coating comprising at least one second member of the color forming set; and
3. Heating to a temperature which during the period of contact and heating is not destructive of the photoconductive substrate or the carrier sheet to form a copy of said particle image on said carrier sheet; said color forming set comprising at least two chemical compounds which will react with each other to form a colored product during the heating period.

2. A method according to claim **1,** wherein the mean grain size of said fine particles is from about 1 to 200 μ.

3. A method according to claim **1,** wherein the amount of the first member adsorbed on the fine particles is from about 1 to 10 parts by weight based on 10 parts by weight of said particles.

4. A method according to claim **1,** wherein the step of depositing comprises cascading the fine particles over the photoconductive layer.

5. A method according to claim **1,** wherein the heating-temperature is from about 50° to 120°C.

6. A method according to claim **1,** wherein the first member is selected from the group consisting of (a) Crystal Violet lactone, (b) dianisidine base, (c) 4-nitro-O-anisidine, (d) Rhodamine lactone, (e) gallic acid, (f) monoethanol amine, (g) 2,3-dihydroxy naphthalene, (h) 8-amino-1-naphthol-5,7,-disulfonic acid, (i) 4-methoxy-1-naphthol, (j) 1-phenyl-3-carboxy pyrazolone, (k) phloroglucinol and (l) 3-hydroxy-1-phenol; the second member is selected from the group consisting of (m) attapulgite clay, (n) ammonium methavandate, (o) copper sulfate, (p) 2-diazo-4-chloro-1-phenol, (q) 4-diazo dipropyl aniline and (r) 4-diazo ethylbenzyl aniline; and the combination of the members is (a) and (m), (b) and (m), (c) and (m), (d) and (m), (e) and (n), (f) and (o), (g) and (p), (h) and (p), (g) and (q), (g) and (r), (i) and (q), (j) and (q), (j) and (r), (k) and (q), and (l) and (r).

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,840,385 Dated October 8, 1974

Inventor(s) SHIGEAKI YOSHIDA

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

Page 1, title page, change name of inventor from:

Shigeaki Yoskida

to read --

Shigeaki Yoshida --

Signed and sealed this 24th day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

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