United States Patent

Notley et al.

[15] **3,653,902**

[45] **Apr. 4, 1972**

[54] PHOTOGRAPHIC MATERIALS

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[22] Filed: **Apr. 28, 1970**

[21] Appl. No.: **32,753**

Related U.S. Application Data

[63] Continuation of Ser. No. 766,356, Aug. 23, 1968, abandoned, which is a continuation of Ser. No. 405,597, Oct. 21, 1964, abandoned.

[52] **U.S. Cl.** .....**96/49,** 96/48 HD, 96/67, 96/75, 96/87 R, 96/91 R

[51] **Int. Cl.** **G03c 5/18,** G03c 1/52

[58] **Field of Search** 96/49, 75, 91, 115

[56] **References Cited**

UNITED STATES PATENTS

3,032,414	5/1962	James et al.	96/49 X
3,143,418	8/1964	Priest et al.	96/91 X
3,260,599	7/1966	Lokken	96/75

FOREIGN PATENTS OR APPLICATIONS

850,954	10/1960	Great Britain	96/49

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Attorney—Cushman, Darby and Cushman

[57] **ABSTRACT**

Vesicular photographic films having, as a vehicle, derivatives of polyvinyl alcohol in which at least 40 percent and preferably at least 75 percent of the alcohol groups are in the form of ester or acetal. The photographic materials are obtained by evaporating solvent from a solution containing the polymer and a light decomposable agent.

8 Claims, No Drawings

PHOTOGRAPHIC MATERIALS

This is a continuation of U.S. Pat. application, Ser. No. 766,356, filed Aug. 23, 1968, which in turn was a continuation of U.S. Pat. application, Ser. No. 405,597, filed Oct. 21, 1964, both applications now being abandoned.

The present invention relates to photography and, more particularly, to the production of vesicular photographic images.

Vesicular images are formed in photographic film by small bubbles or vesicles of gas which are formed and trapped in areas of the film exposed to light and which refract light. Generally speaking, the film has a colloid or a resin coating or vehicle on a backing material and a light-sensitive agent or sensitizer, most commonly a diazo compound, dispersed throughout the coating. When the film is exposed to light, the sensitizer releases molecules of a gas-nitrogen in the case of diazo compounds. These ordinarily do not form vesicles immediately, but they do so when the film is heated, presumably because the vehicle is relaxed sufficiently on heating for the gas molecules to diffuse together into bubbles and for the bubbles to expand. The resulting vesicles make the vehicle opaque to transmission of light in the exposed areas and also reflect light and scatter light so that they appear white.

The early vesicular materials employed gelatin as a vehicle, in part because they had been known earlier and used with diazo sensitizers, in wet development using dye coupling. These vehicles suffered from the difficulty that the vesicular images obtained faded rapidly. Later work has revealed that this problem was caused, at least partly, by the sensitivity of gelatin to water. Gelatin absorbed moisture from the air and became soft, thus collapsing the vehicle and destroying the image.

An improvement in vesicular photography which avoided this difficulty is described in James et al. U.S. Pat. No. 3,032,414 in which the vehicle is a water-insensitive resin material which is made into a film by dissolving it in an organic solvent with the sensitizer, applying it to a backing and drying.

Another difficulty with earlier vesicular record materials is sensitivity of the developed image to high temperature. Normally, the image is preserved because the vehicle is rigid and the vesicles are immobile. The rigidity of the vehicle is reduced during development to permit gas molecules to diffuse together to form the vesicles and for expansion of the vesicles, but it is thereafter restored by cooling to give permanency to the image. To be truly permanent, the vehicle must remain rigid under the conditions in which it is stored and handled, such as heat and moisture.

Certain vehicles which avoid the aforesaid heat and moisture sensitivity problems are described in prior U.S. Pat. applications of Parker and Mokler Ser. No. 192,067 and Ser. No. 173,342 filed May 3, 1962 and Feb. 15, 1962, respectively, and of Daech application, Ser. No. 191,288, filed Apr. 30, 1962 Ser. No. 192,067 is now U.S. Pat. No. 3,161,511, Ser. No. 173,342 is now abandoned and Ser. No. 191,288 is now U.S. Pat. No. 3,189,455. Ser. No. 386,755, which is a CIP of Ser. No. 173,342, is now U.S. Pat. No. 3,251,690. In the search for other vehicles having these advantageous properties, it now has been found that certain polymers of vinyl esters and acetal derivatives of polyvinyl alcohol may be used as vehicles for vesicular photographic films, and provide excellent heat- and moisture-resistant images.

It has been suggested to utilize polyvinyl acetals as vehicles when combined with modifying resins to adjust their permeability to nitrogen to the appropriate range. In addition, the copending application of Norman T. Notley, et al., Ser. No. 403,633 filed Oct. 13, 1964 for PHOTOGRAPHIC MATERIAL, describes the use of polyvinyl acetals and polyvinyl esters as vehicles in mixture with certain other resins to facilitate controlling photographic sensitivity and contrast now abandoned. Ser. No. 768,943, which is a continuation of Ser. No. 403,633, is now U.S. Pat. No. 3,498,786.

In accordance with the present invention, it has been found that certain polyvinyl acetals and polyvinyl esters may be utilized alone as vehicles without modifiers or other resins.

The polymers which may be used in accordance with the present invention are polymers of vinyl esters and polyvinyl acetals. The polyvinyl esters are obtained by polymerization of esters of vinyl alcohol with aliphatic or aromatic carboxylic acids. The aliphatic acid esters are preferred, the most suitable being lower fatty and unsaturated acids containing up to about six carbon atoms, such as acetic acid, propionic acid, valeric acid, vinyl acetic acid or crotonic acid. However, higher fatty acids such as octanoic acid may be used, particularly in combination with lower fatty acids. Suitable aromatic acids include benzoic acid, naphthoic acids and phenyl acetic acid. The ester polymers may be obtained from the monomers by any conventional polymerization method, i.e., in bulk, solution, or aqueous emulsion or dispersion, in the presence of, e.g., a free radical or ionic catalyst, the details of which form no part of the present invention.

Polyvinyl acetals are generally made by reaction between aldehydes and polyvinyl alcohol or polyvinyl esters, such as polyvinyl acetate. It is preferred that saturated lower aliphatic aldehydes be employed containing up to six carbon atoms, particularly butyraldehyde and formaldehyde. However, small amounts of higher aliphatic aldehydes or aromatic aldehydes such as benzaldehyde may be included. The polyvinyl acetal polymers may contain small amounts of residual hydroxyl groups which have not been converted to the acetal derivative. However, no more than about 60 percent and preferably no more than about 25 percent of the hydroxyl groups should remain as free hydroxyl groups, i.e., not in the form of acetal or ester.

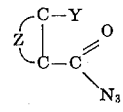
It will be appreciated that while the above description of preferred polymers has been directed to homopolymers, copolymers containing more than one acetal or ester group may be used. Thus polyvinyl acetals may contain two or more types of acetal groups or, e.g., acetate units as well as acetal. In addition, relatively minor amounts of other ethylenically unsaturated monomers containing one or more

groups may be present, e.g., up to about 5 percent as long as the characteristics of the polymer are essentially not altered so as to render it unsuitable.

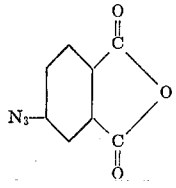
Any suitable substrate may be employed for the photographic materials. For films, the preferred materials are films of Mylar (polyethylene terephthalate) polyethylene and polypropylene. Paper backings, metal plates and glass slides also are useful for certain applications. Thus, while films are referred to herein, it will be understood that the invention embraces any backing layer.

The above polymers are substantially uniformly blended with a light decomposable agent, or sensitizer, of the types which are known in the art of vesicular photographic materials which, upon exposure to light, decompose into products which are volatile upon warming to form the above-described radiation scattering cavities. The preferred sensitizers are nonreactive to the vehicle and, upon exposure to light, decompose into products which are chemically non-reactive to said vehicle and which are volatile to form radiation scattering discontinuities only in the light struck areas in said vehicle to thereby furnish a record. Of these preferred sensitizers, those which are especially useful are of the type which decompose to release nitrogen on exposure to light, particularly the diazonium salts. Suitable sensitizers include the diazo compounds which release nitrogen on exposure to light as disclosed in U.S. Pat. Nos. 3,032,414, 2,923,703 and 2,976,145, for example, p-diazo diphenyl-amine sulfate, p-diazo diethylaniline zinc chloride, p-diazo ethyl hydroxyethylaniline zinc chloride, p-diazo ethyl methyl aniline zinc chloride, p-diazo diethyl methyl aniline zinc chloride, p-diazo ethyl hydroxyethylaniline zinc chloride, 1 diazo-2 oxy naphthaline-4 sulfonate, d-diethyl amino benzene diazonium chloride $ZnCl_2$, 4-benzolamino-2-5-diethoxy benzene diazonium chloride, p-chlorobenzene-sulfonate of 4-diazo-1 cyclohexylaniline, p-chlorobenzene-sul-

fonate of 4-diazo-2-methoxy-1-cyclo-hexylamino benzene, tin chloride double salt of 4-N-methylcyclohexyl-amino-benzene diazonium chloride, p-acetamino benzene diazonium chloride, 4-dimethylamino benzene diazonium chloride, 3-methyl-4-diethyl amino benzene diazonium chloride, 4-morpholino benzene diazonium chloride, 4-piperidyl 2-5-diethoxy benzene diazonium chloride, 1-dimethyl amino naphthaline-4-diazonium chloride, 4-phenyl amino diazo benzene diazonium chloride. Other useful sensitizers are those disclosed in British specification, No. 956,336 published Apr. 22, 1964 and having the general formula



in which Y represents hydroxyl, amino, alkylamino, arylamino, or mercapto and Z represents the atoms necessary to form a cyclic structure, and those disclosed in French Pat. No. 1,281,905 having the general structure



The amount of diazonium salt or other sensitizer generally is quite low, not above about 20 percent and preferably in the range 1–20 percent of the weight of the polymer.

The vehicle and the sensitizer may be combined by any suitable method. However, it is preferred that they each be dissolved in a solvent and the resultant solutions combined. In this embodiment it is only necessary that the respective solvents be mutually miscible. For the most part, polar solvents will be used such as alcohols, ketones, nitriles, esters, ethers and halogenated solvents. Particularly useful are methyl, ethyl and isopropyl alcohols, alkyl acetates, acetone, methyl ethyl ketone, dioxane and acetonitrile. However, any inert solvent which meets the above miscibility requirement may be used.

After the film is thus prepared, there are at least three different methods of processing it. In one form, the film is exposed to image forming light, e.g., by being placed in contact with a transparency and exposed to light passing through the transparency, then the film is heated to 160°–300° F. for 1/10 to 3 seconds. This will produce an image of the opposite photographic sign from the transparency. Thus if the transparency is negative, a positive vesicular photograph will result.

A second processing system which can be used is that described in U.S. Pat. No. 2,911,299. In it, the film is exposed to image forming light and gas released by the sensitizer is allowed to diffuse from the vehicle at a temperature too low for development to take place. Then the film is exposed overall to uniform light which actuates undecomposed sensitizer, and it is heated to cause development at 160°–300° F for 1/10 to 3 seconds either during or shortly after the second exposure, but before the gas has substantially diffused from the film. This results in image formation in areas not originally struck by light and an image of the same photographic sign as the transparency. Thus a negative transparency results in the formation of a negative vesicular photograph which might be called a reversal image or a direct image.

The third processing system is that described in U.S. application, Ser. No. 383,169 filed July 16, 1964 now abandoned. Ser. No. 533,743, which is a CIP of Ser. No. 383,169, is now U.S. Pat. No. 3,457,071. In that system, the film is exposed to image forming light of relatively low intensity for at least about 0.5 second and preferably for at least about 2.0 seconds. That is, the light is of low enough intensity that the film does not receive a normal exposure in less than 0.5 second and preferably 2.0 seconds. Then the film receives an overall exposure of light intensity which is sufficient to expose the film in less than 0.2 second and preferably less than 0.01 second. Overexposure or longer exposure can be tolerated, but there must be sufficient light to properly expose the film during the indicated time. This procedure avoids a separate diffusion step as used in the method of U.S. Pat. No. 2,911,299. In some cases, no heating is required to cause development, and the image appears spontaneously. However, in other cases, some heating may be used to advantage, as more fully described in application, Ser. No. 383,169.

The invention is illustrated in the following examples, all parts being by weight:

EXAMPLE 1

25 gms. of formaldehyde polyvinyl acetal of composition, 82 percent acetal content, 9.5–13.0 percent acetate content and 5.0–6 percent hydroxyl content, was dissolved in 200 gms. of 1,4-dioxane to produce a solution A. A separate solution B was made from 2.7 gms. of p-Diazo N,N-Dimethyl Aniline Boro-Fluoride Salt, 64 gms. of methanol and 20 gms. of Distilled H_2O. The two solutions were mixed thoroughly and were then coated onto a Mylar backing by means of a Gardner film coating knife and a Bird vacuum plate. The film was then processed by first exposing through an image bearing transparency for about 10 seconds to a 100 watt ultraviolet lamp (General Electric No. H100A4–IT) spaced about 3 inches from the film and immediately thereafter to a flash lamp (General Electric 200 watt second and within a polished reflector, the film being at the edge of the reflector and about 3 inches from the flash tube, the flash duration being 1/1500 second.) The images obtained showed a maximum projection density of 2.70 and a minimum of 0.20.

Examples 2–4 are compositions which were prepared, coated on Mylar and exposed as in Example 1, with approximately the same results.

EXAMPLE 2

Solution A	
Formaldehyde Polyvinyl Acetal (50% Acetal, 40–50% Acetate, 5.0–6% Hydroxyl)	25
Methyl Ethyl Ketone	10
Solution b	
P-Diazo-N,N—Dimethyl Aniline Boro Fluoride Salt	3
Acetonitrile	35

EXAMPLE 3

Solution A	
Butyraldehyde Polyvinyl Acetal (80% Acetal, 0-1.0% Acetate, 18.0–20.0% Hydroxyl)	25
1,4-Dioxane	260
Solution B	
p-Diazo N,N—Dimethyl Aniline zinc chlordie	4.2
Acetonitrile	35

EXAMPLE 4

Solution A	
Butyraldehde Polyvinyl Acetal (80% Acetal, 0–2.5% A Acetate, 18–20% Hydroxyl)	25
1,4-Dioxane	125
Solution B	
p-Diazo N,N—Dimethyl	

Aniline Zinc Chloride	
i Salt	4
Acetonitrile	40

EXAMPLE 5

The following composition was prepared and coated on Mylar as in Example 1.

Solution A	
Formaldehyde Polyvinyl Acetal (82% Acetal, 9.5–13.0$ % Acetate 5.0–6.0% Hydroxyl)	25
1,4Dioxane	50
Solution B	
p-Diazo N,N-Dimethyl Aniline boro Fluoride Salt	2
Acetonitrile	43

Samples were exposed as in Example 1 and useful images were obtained.

EXAMPLE 6

a composition having the following constituents was prepared and coated on Mylar as described in Example 1.

Solution A	
Butyraldehyde Polyvinyl Acetal (88% Acetal, 0–2.5% Acetate, 9.0–13.0% Hydroxyl)	25
1,4-Dioxane	200
Solution B	
p-Diazo N,N-Dimethyl Aniline Zinc Chloride Salt	4.2
Acetonitrile	35.2

Two groups of samples were exposed successively for 2.0 and 1/1500 second as described in Example 1. One group of samples was heated gently to about 120° F. during the second exposure while the other group was not. The minimum projection density was 0.2 for the samples which had been heated as compared with 0.6 for those which had not.

EXAMPLE 7

A solution was made from the following ingredients:

	Parts
Formaldehyde Polyvinyl Acetal (70% Acetal, 22–30% Acetate and 5.5–7.0% Hydroxyl)	25
Diphenyl Phthalate	2.5
1,4-Dioxane	200
p-Diazo N,N-Dimethyl Aniline zinc Chloride Salt	4
Acetonitrile	40

The solution was applied to a glass plate and dried. The resultant plate was then exposed to light from a mercury arc lamp (100 watt H100–A4) for 10.0 seconds passing through a transparency, and it was then developed by heating to 240° F. for 2 seconds. An image was obtained showing a maximum projection density of 2.65.

It can be seen from the foregoing example that it is possible to include a small amount of a plasticizer for the polymer without rendering the vehicle unsuitable.

EXAMPLE 8

Example 1 was repeated except that the film was exposed through an image bearing transparency for 10 seconds to a 100 watt ultraviolet lamp spaced 2 inches from the film and the film was then developed by heating at 240° F. for 2 seconds. A useful image was obtained.

In examples 9, 10 and 11 the materials described were employed in making of the film and exposed and developed in the manner described in Example 8. In each case a useful image was obtained.

EXAMPLE 9

Gelva V–60	25
Methyl Ethyl Ketone	100
p-Diazo-N,N-Dimethyl Aniline zinc Chloride Salt	4
Acetonitrile	40

Gelva V–60 is a homopolymer of vinyl acetate supplied in the form of granules whose viscosity is 54–66 cps in benzene solution containing 86 grams of resin per 1000 ml. of solution, determined at 20° C. with an Ostwald-Cannon-Fenske viscometer, molecular weight (wt av) is 300,000, softening point is 385° F. (determined by a modified Kraemer and Sarnow method using 10 grams of mercury over a 6.35 mm. cylindrical plug of Gelva Resin in a 7 mm. diameter glass tube), heat seal temperature is 185°–195° F. (The minimum temperature required for heat sealing of a 1–1.5 mil (dry) film cast from methanol solution on ditto paper dried at room temperature for 45 minutes, then force dried for one hour at 70° C. conditioned for 16 hours at 73° F., 50 percent R.H., using a PACK-RITE 1.5 sec. dwell, 10 psi pressure, on 4 inch × ¾ inch sample, face to face), maximum tensile strength is 6500 p.s.i. (molded specimens —— 2⅜% inch gauge × ¼ inch × 0.07 inch — conditioned 48 hours at 73° F., 50% R.H. Instron Tester at 2 in./min. crosshead speed) percent elongation at yield is 4.8, abrasion resistance is 59 mg. weight loss (Taber abrasion in mg loss/1000 revs on cast film conditioned 48 hours at 73° F., 50% R.H., C–10 wheels — 1000 gm. load), and second order transition temperature is 27° C.

EXAMPLE 10

Gelva V–100	25
Methyl Ethyl Ketone	100
p-Diazo-N,N-Dimethyl Aniline Zinc chloride Salt	4
Acetonitrile	40

Gelva V100 is a homopolymer of vinyl acetate supplied in the form of granules whose properties, determined by the methods stated for Gelva V60 are as follows: viscosity, 90-110 cps; molecular weight, 500,000; softening point, 446° F.; heat seal temperature, 195°–205° F.; maximum tensile strength, 7200 p.s.i.; percent elongation at yield, 4.6; abrasion resistance, 64 mg. weight loss; second order transition temperature, 28° C.

EXAMPLE 11

Gelva V–800	25
Methyl Ethyl Ketone	ϕ
p-Diazo-N,N-Dimethyl Aniline Zinc chloride Salt	4
Acetonitrile	40

Gelva V–800 is a homopolymer of vinyl acetate supplied in the form of granules whose properties, determined by the methods stated in Example XII for Gelva V–60 are as follows: Viscosity, 700–1000 c.p.s.; molecular weight, about 1.5×10^6; heat seal temperature, 205°–215° F.; maximum tensile strength, 7300 p.s.i.; percent elongation at yield, 4.3; abrasion resistance, 59 mg. weight loss; second order transition temperature, 29° C.

The invention now having been described by reference to specific preferred embodiments, it will be appreciated that various changes may be made in details regarding the materials and the method of using them without departing from the scope of the invention, this being as defined in the claims.

We claim:

1. A method of preparing vesicular images comprising:

exposing to image forming light a photographic material capable of furnishing a record solely in the form of a distribution pattern of radiation scattering discontinuities formed within an otherwise substantially homogenous vehicle, said material being in the form of a dry, water-resistant non-hygroscopic film, the continuous phase of said film consisting essentially of a synthetic, water-insoluble, non-water swelling highly linear thermoplastic formaldehyde polyvinyl acetal consisting essentially of vinyl formal units, vinyl alcohol units and units of vinyl ester with a fatty acid containing up to six carbon atoms, at most 25 percent of said repeating units being vinyl alcohol and at least 50 percent of said repeating units being vinyl formal, and a light decomposable solid agent substantially uniformly dispersed therein as the sole essential decomposable agent, said decomposable agent itself being non-reactive to said vehicle and, upon exposure to light, decomposing into products which are chemically non-reactive to said vehicle and which upon warming form said radiation scattering discontinuities only in the light struck areas in said polymer to thereby furnish said record, said photographic material being obtained by combining said polymer and said decomposable agent in non-aqueous organic solvent for them to form a uniform, essentially water-free mixture thereof and forming the photographic material by removal of said solvent, and thereafter heating said photographic material to develop a vesicular image.

2. a method as set forth in claim 1 in which said light-decomposable agent is a diazo compound.

3. A method as set forth in claim 1 in which the film is heated to cause development to a temperature of 160°–300° F. for 1/10 –3 seconds.

4. A method of preparing vesicular images comprising:

exposing to image forming light a photographic material capable of furnishing a record solely in the form of a distribution pattern of radiation scattering discontinuities formed within an otherwise substantially homogeneous vehicle, said material being in the form of a dry, water-resistant non-hygroscopic film, the continuous phase of said film consisting essentially of a synthetic, water-insoluble, non-water swelling highly linear thermoplastic formaldehyde polyvinyl acetal consisting essentially of vinyl formal units, vinyl alcohol units and units of vinyl ester with a fatty acid containing up to six carbon atoms, at most 25 percent of said repeating units being vinyl alcohol and at least 50 percent of said repeating units being vinyl formal, and a light decomposable solid agent substantially uniformly dispersed therein as the sole essential decomposable agent, said decomposable agent itself being non-reactive to said vehicle and, upon exposure to light, decomposing into products which are chemically non-reactive to said vehicle and which upon warming form said radiation scattering discontinuities only in the light struck areas in said polymer to thereby furnish said record,

said photographic material being obtained by combining said polymer and said decomposable agent in non-aqueous organic solvent for them to form a uniform, essentially water-free mixture thereof and forming the photographic material by removal of said solvent,

diffusing said volatile products from said vehicle without forming an image therein,

subjecting said vehicle to substantially uniform irradiation to cause decomposition of an additional quantity of said decomposable agent, and

heating said photographic material to cause development and the formation of a vesicular image.

5. A method as set forth in claim 4 in which said light-decomposable agent is a diazo compound.

6. A method as set forth in claim 4 in which the film is heated to cause development to a temperature of 160°–300° F. for 1/10 –3 seconds.

7. A vesicular photographic material capable of furnishing a record solely in the form of a distribution pattern of radiation scattering discontinuities formed within an otherwise substantially homogeneous vehicle, said material being in the form of a dry, water-resistant, non-hygroscopic film, the continuous phase of said film consisting essentially of a synthetic, water-insoluble, non-water swelling highly linear thermoplastic formaldehyde polyvinyl acetal consisting essentially of vinyl formal units, vinyl alcohol units and units of vinyl ester with a fatty acid containing up to six carbon atoms, at most 25 percent of said repeating units being vinyl alcohol and at least 50 percent of said repeating units being vinyl formal, and about 1–20 percent, based on the weight of said polymer, of a light decomposable solid agent substantially uniformly dispersed therein as the sole essential decomposable agent, said decomposable agent itself being non-reactive to said vehicle and, upon exposure to light, decomposing into products which are chemically non-reactive to said vehicle and which upon warming form said radiation scattering discontinuities,

said photographic material being obtained by combining said polymer and said decomposable agent in non-aqueous organic solvent for them to form a uniform, essentially water-free mixture thereof and forming the photographic material by removal of said solvent.

8. A vesicular photographic material as set forth in claim 7 in which said light decomposable agent is a diazo compound.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,653,902 Dated April 4, 1972

Inventor(s) Norman T. Notley and Irwin M. Senentz, Jr.

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

Column 4, line 47, change "10" to -- 100 --

Column 6, line 56, change "ϕ" to -- 100 --

Column 6, line 63, change "XII" to -- 9 --

Signed and sealed this 19th day of December 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE 1969 O-366-334