

1

2

3,684,675

ELECTROPHORETIC PROCESS FOR COATING PHOTOGRAPHIC LAYERS

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8 Claims

ABSTRACT OF THE DISCLOSURE

Photographic elements incorporating an electrically-conducting support having coated thereon at least one radiation-sensitive silver salt layer can be prepared with little or no hydrophilic colloid binder by electrophoretic deposition of dispersed preformed silver salt crystals from a liquid medium, which electrophoretic coating process can also be used to deposit photosensitive silver salts previously dispersed in a hydrophilic colloid binder.

This invention relates to photography and more particularly to photographic elements having, as the light-sensitive component, a substantially binder-free layer of silver halide crystals and to a process for preparing both such elements and additional elements utilizing hydrophilic colloid binders.

Conventional photographic elements employ a support material coated with a photographic emulsion that typically includes photosensitive silver halide crystals dispersed in a hydrophilic colloid such as gelatin. In many instances, gelatin or another hydrophilic colloid is an advantageous constituent of a photographic element. The use of a hydrophilic colloid binder to promote adequate adhesion between the photosensitive species and the support, however, can be attended by certain related disadvantages that pertain to various photographic situations. Typical binder colloids absorb light of short wavelengths (e.g. ultraviolet rays); as such, the binder material can determine the short wavelength limit of usefulness for any given photographic element. Such a condition operates to impede preparation of high quality, ultraviolet-sensitive photographic elements such as those used in astronomical studies. Moreover, developing agents are required to penetrate the colloid in order to develop a photographic image on the photosensitive material. Additionally, the hydrophilic colloid tends to attract moisture which can adversely affect the stability and image producing capability of the photographic element, and special measures must be taken to insure adequate adhesion between the normally hydrophobic support and the hydrophilic colloid binder. To avoid the use of a colloid binder, it is known to prepare photographic elements having thin, binder-free layers of microcrystalline silver halide coated by vacuum deposition techniques wherein the silver halide crystals are formed in situ on the support. Such coating means, however, require specialized apparatus to carry out the coating operation in a sealed system under conditions of elevated temperature and reduced pressure. Additionally, the binderless, microcrystalline silver halide layers so deposited are subject both to non-uniform photographic response and to deterioration upon storage, the deterioration generally resulting from such factors as pressure-caused abrasion fog.

Accordingly, it is an object of this invention to provide new, substantially binder-free silver salt photographic elements.

Another object of the present invention is to provide a novel process for preparing both substantially binder-free silver salt photographic elements and photographic elements incorporating a hydrophilic colloid.

Additional objects and advantages will become apparent from a reading of the following specification and appended claims.

The objects of the present invention are accomplished both with an electrophoretic coating process for preparing photographic elements having an electrically-conducting support having thereon a radiation-sensitive layer including preformed, radiation-sensitive silver salt crystals which process includes:

- 5 (A) Dispersing radiation-sensitive silver salt crystals in a liquid medium,
- 10 (B) Immersing a portion of each of a pair of electrodes in the silver salt dispersion in a spaced relationship with the remaining electrode (and advantageously in a parallel spaced relationship), and
- 15 (C) Applying a D.C. potential across said pair of electrodes,

whereupon radiation-sensitive silver salt crystals are deposited upon an electrode of said electrode pair, which electrode is the support for said photographic element.

The term "radiation-sensitive," as utilized herein, is descriptive of chemical species (silver salts) that are activated by exposure to electromagnetic radiation to typically provide latent images that can be intensified by various photographic development techniques to provide visible images. The subject silver salts are radiation-sensitive and include species that are light-sensitive. However, "radiation-sensitive" comprehends responsiveness to activating radiation both within and without the visible portion of the spectrum. In addition to photosensitivity or visible light sensitivity, radiation-sensitive refers to the responsiveness of an activatable silver salt species to a wide segment of electromagnetic radiation including, for example, x-radiation, ultraviolet rays, infrared radiation and the like.

The preformed, radiation-sensitive silver salt crystals used in the practice of this invention include those of the silver halides typically employed in gelatino-silver halide photographic emulsions, such as silver bromide, silver chloride and silver iodide. Additionally, mixtures of these halides are advantageously utilized, as are co-crystals such as, for example, silver bromoiodide, silver chlorobromide, silver chloroiodide and the like silver halides.

The silver halide crystals that function as silver salts of this invention include sensitized silver halides that have been spectrally sensitized to additional portions of the radiation spectrum, conventionally with sensitizing dyes such as cyanine dyes, carbocyanine and the like polymethine cyanine dyes including complex (trinuclear) cyanines, merocyanine dyes including complex (trinuclear) merocyanines, styryl dyes, oxonol dyes, as well as additional dye sensitizers like substituted polycyclic quinones, pyrylium compounds and the like. Still additional spectral sensitizers are well known in the art. Spectrally sensitized silver halides can be dispersed in combination to obtain a composite dispersion containing silver salt crystals sensitized to record various portions of the spectrum and generally to visible red, green and blue light rays via the use of cyan, magenta and yellow sensitizing dyes. Such multiple sensitization in a common dispersion is conventionally termed a "mixed grain" dispersion or coating.

Additionally, the silver salts useful herein include crystalline silver-sensitizing dye complexes which are the complex reaction product of a substantially water soluble silver salt and a spectral sensitizing dye. The noted silver-dye complexes are conveniently prepared by admixing the dye and the silver salt and are conventionally predispersed in a hydrophilic colloid, e.g. gelatin, prior to coating on a support. Particularly advantageous silver salts include those of the more highly solubilizing anions, and especially

5

form coating is desired, is advantageously a parallel spaced relationship, and with the immersed electrode surface being that on which electrophoretic deposition occurs. An electrical potential is impressed across the two electrodes, typically at a point on each electrode that is not immersed in the dispersion. As current flows in the dispersion between the two electrodes, dispersed silver salt crystals such as silver halide crystals migrate to and are deposited upon one of either the cathode or the anode of the electrode pair, depending upon the polarity of the electrical double layer at the silver halide medium interface, which polarity derives from the particular choice of dispersion medium, dispersed phase and surface active agent, if used.

The electrodes used herein can be either electrically-conducting materials or other materials having an electrically-conducting layer coated thereon. Conventional electrodes include plates and foils fabricated from stainless steel, iron and other conducting metals and alloys, as well as tin oxide coated glass, gold coated on chromium subbed glass, and titanium and gold coated on photographic film base such as flexible resinous film base materials such as cellulose acetate, cellulose butyrate, polyvinylbutyral, polystyrene, poly(ethylene terephthalate) and the like. Other metal coated support materials and additional conducting materials are known to those skilled in the art. In the practice of this invention, the electrodes are partially immersed in the dispersion so that they are not in mutual contact. It is preferred that the conducting faces of the subject electrodes are oriented towards each other in the dispersion, and although one can uniformly electrophoretically deposit a dispersant such as silver halide on curved surfaces, the electrodes herein are typically flat plates disposed in a parallel arrangement with facing conducting surfaces equidistantly separated at all points. This preferred orientation ensures a uniform coating thickness as well as providing a composite, coated element that is well-suited for conventional photographic purposes. Other orientations and surface geometries can be used where desired for particular purposes.

The distance separating the electrodes is subject to variation, with increased separations requiring higher voltages applied between the electrodes to promote advantageous deposition. Generally, the subject electrodes are maintained in the dispersion at a separation of from about 5 to 10 millimeters, but wider variations can be used for larger scale coating operations. To cause electrophoretic deposition of the dispersed silver halide crystals, a D.C. electrical potential is applied across the electrodes between points on each that typically are not immersed in the dispersion. Upon completing an electrical circuit, the dispersed particles migrate to either the cathode electrode or the anode electrode, depending upon the polarity of the interfacial electrical double layer between the dispersed phase and the medium. For any particular silver salt dispersed phase, the electrical potential that is required to initiate and sustain deposition can vary widely depending upon the dispersion medium. In general the rate of deposition increases with increasing applied potential.

It is advantageous, therefore, to choose an electrical potential such that the rate of deposition can be conveniently controlled. An electrical potential that is too strong can contribute to unwanted electrical discharge such as arcing between the electrodes. Conventionally, potentials of from about 50 to about 1500 volts D.C. are used, but factors such as dispersion composition, electrode separation, desired coating thickness, etc., exert an influence upon the most suitable electrical potential. For particular situations, higher or lower D.C. potentials can be advantageously employed. If multiple layers are electrophoretically deposited in sequence, according to the subject invention, each subsequent layer typically requires a higher electrical potential to ensure advantageous deposition.

As current flows between the electrodes, a silver salt

6

or mixture of silver salts such as those described herein-above is deposited upon one of the electrodes according to the electrophoretic mechanisms described above. The rate and the electrode at which the silver salt deposition is obtained can be determined empirically and when the desired coverage is obtained, the source of electrical potential is disconnected from the electrodes. The electrode upon which silver salt has been deposited then functions as the support material for the composite, radiation-sensitive photographic element so prepared.

After a completely prepared photographic element is removed from the dispersion and dried, it can be image-wise exposed, developed and fixed or otherwise stabilized to yield a permanent photographic silver image. Exposure is to a suitable radiation source, e.g., X-rays, visible light, ultraviolet light, etc., whereupon a metallic silver latent image is produced in the electrophoretically deposited silver salt layer. Developing the latent image to a visible photographic silver image is accomplished in the case of monochromatic elements by treating the image-wise exposed photographic element with a photographic developing composition. Such developing compositions incorporate a silver halide developing agent, typically polyhydroxy benzenes like hydroquinones, catechols and pyrogallols, as well as other polyhydroxy compounds such as ascorbic acid. Additional developing agents include aminophenols, p-phenylenediamines and 3-pyrazolidones. Exemplary of silver halide developing agents that are advantageously used herein are compounds like 2-methyl-3-chlorohydroquinone, bromohydroquinone, catechol, 5-phenylcatechol, pyrogallol monomethylether (1-methoxy - 2,3 - dihydroxy benzene), 5-methylpyrogallol monomethylether isoascorbic acid, N-methyl-p-aminophenol and dimethyl-p-phenylene diamine.

Subsequent to development, the photographic silver image is stabilized by treatment with a photographic fixing bath including a fixing agent to remove undeveloped silver salt. Conventional fixing agents or silver halide solubilizing agents include water-soluble thiosulfates, thiocyanates and mercaptans such as ammonium thiosulfate, sodium thiocyanate and the disodium salt of 2-mercapto-4-hydroxy-5-aminopyrimidine. A particularly preferred fixing agent is sodium thiosulfate. Stabilization is generally accomplished by treatment with a fixing bath that incorporates a fixing agent such as those mentioned previously. Exemplary of fixing baths is one having the formula:

Sodium thiosulfate	-----g--	240
Sodium sulfite (desiccated)	-----g--	15
Acetic acid (28% aqueous)	-----cc--	48
Boric acid (crystals)	-----g--	7.5
Potassium alum	-----g--	15
Water to make		1000 cc.

Where mixed grain elements are prepared, such as those described herein that are suited to the production of full color images, processing is advantageously carried out according to the technology of color reversal processing such as is described in U.S. 2,614,925.

A mixed grain dispersion suitable for deposition according to the present invention to prepare a full color photographic element can be made by codepositing silver halide grains that are spectrally sensitized to record particular light ranges. Such grains are advantageously pre-dispersed in a hydrophilic colloid. For example, silver chlorobromide grains that are sensitized to record red light by a photographic spectral sensitizing dye can be dispersed in a suitable medium, such as those described herein along with silver bromide grains that are sensitized to record green light by a photographic spectral sensitizing dye. The codispersed silver halide grains can then be electrophoretically deposited on a conducting support according to the above-described procedures of the subject invention. Unsensitized silver halide grains treated with a yellow filter dye can then be electrophoretically deposited in a second blue-sensitive layer over and con-

7

tiguous to the first described layer containing silver halide sensitized to record light of the red and green portions of the spectrum. Such a composite element upon image-wise exposure and processing produces full color photographic images.

Alternatively, a mixed grain emulsion of the type described in U.S. Pat. 2,388,859 can be prepared according to the electrophoretic coating process of the subject invention. One photosensitive layer is electrophoretically deposited, such a layer including fast silver halide grains sensitized to record the blue spectral region and slow silver halide grains sensitized to record the red and green spectral regions. The sensitivity of the grains primarily sensitive to blue light is considerably greater than the blue light sensitivity of either the red or the green sensitized silver halide grains. Over and contiguous to the photosensitive layer can be advantageously coated by conventional means, a yellow colored filter layer which absorbs enough blue light so that the speed of the fast blue sensitive component of the mixed grain emulsion is reduced to a value equivalent to those of the red and green speeds of the two other components. Where the blue speed differential between the fast and slow emulsions is, for instance, as great as fifty times, a yellow filter absorbing 98% of the overall blue light may be used. Such a filter is one containing a dye of the pyrazolone type exemplified by tartrazine. This filter would reduce the blue speed of the red and green sensitive components of the mixed grain emulsion to approximately 2% of the speeds of the red and green thereby rendering the blue sensitivity of these grains negligible for printing purposes. The high speed blue sensitive emulsion still prints the blue record at the same speed required for printing the red and green records onto the other two components. This yellow filter layer can be, for example, flow coated from an aqueous gelatin solution subsequent to electrophoretically depositing the photosensitive silver halide grains.

A mixed grain element prepared as described herein can be imagewise exposed and developed in a conventional silver halide developing composition to produce a negative silver image. Exemplary of such a developer is one having the formula:

N-methyl-p-aminophenol sulfate	6	G.
Hydroquinone	10	
Sodium sulfite	50	
Sodium carbonate	30	
Potassium bromide	5	
1-phenyl-5-mercaptop tetrazole	0.01	
Water to 1 liter.		

The element after negative development has a negative silver image produced by the blue exposure, a negative silver image produced by the green exposure and a negative silver image produced by the red exposure. In each layer, there remain unexposed and undeveloped grains having the three recited light sensitivities.

After washing, the film can then be light exposed through the base through a red filter transmitting light of longer wavelength than about 640 millimicrons, to expose the residual red sensitive grains and can then be developed in a color-forming developer which can have the following composition:

(A)

p-Aminodiethylaniline HCl	2
Sodium sulfite	6
Sodium carbonate	50
Potassium bromide	5
Potassium thiocyanate	1
Water to 950 cc.	

(B)

o-Hydroxy diphenyl	3
Sodium hydroxide	5
Water	50

8

(For use, Solution B is added to Solution A.)

The film can then be exposed from the support side to green light to expose the residual green sensitive grains and the film can then be developed in a developer which may have the following composition:

(A)

p-Aminodiethylaniline HCl	1½
Sodium sulfite	1
Potassium bromide	2
Water to 950 cc.	

(B)

1-(p-nitrophenyl)-3-methyl-5-pyrazolone	3
Water	50

(For use, Solution B is added to Solution A.)

The film can then be exposed to white light to expose the residual blue sensitive silver halide grains and developed in a developer which may have the following composition:

(A)

p-Aminodiethylaniline HCl	1
Sodium sulfite	1
Potassium thiocyanate	1
Water to 990 cc.	

(B)

Acetoacetanilide	10
Sodium hydroxide	1
Water	10

(For use, Solution B is added to Solution A.)

After development in the yellow color-forming developer, the film is washed and bleached in a solution having a formulation such as the following composition:

Potassium ferricyanide	50
Ammonium hydroxide (28% solution)	2½
Potassium bromide	5
Water to 1 liter.	

The bleaching converts silver metal to a soluble silver salt. The film is then typically fixed for about 5 minutes in hypo, washed for several minutes to remove residual silver salts including silver halide and the soluble silver salts resulting from the ferricyanide bleach, and dried in warm air. After processing and drying the mixed-grain photographic element, the electrode support material carries a visible photographic dye image that is stable and can be viewed either by reflected light or by transmitted light such as by projection when the support material is itself transparent, as in the case of glass, poly(ethylene terephthalate), polystyrene, cellulose acetate and other conventional polymeric resins used as photographic film base materials, and has a transparent conducting layer, if present.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

An aqueous dispersion containing approximately 1 mole AgBr and 12 g. gelatin per kg. in the liquid state at 40° C. is centrifuged and the aqueous supernatant solution is decanted. The silver bromide is washed three times in isopropanol and four times in nitromethane and is finally dispersed in nitromethane. The final volume is approximately the same as the initial volume. Each washing step is accomplished by dispersing the AgBr in the wash liquid, centrifuging and decanting the spent liquid. A sample of this dispersion is diluted to 20 times its volume in nitromethane and placed in a glass beaker thermostated at 75° F. The dilute dispersion is stirred with a poly(tetrafluoroethylene) coated magnetic stirring bar and is irradiated with ultrasonic energy just prior to the preparation of a silver bromide coating. Glass plates, about 2 x 7 x 0.15 cm., coated on one side with chromium, are used as both the cathode and anode. Two electrodes are positioned with

9

their metal coated sides parallel to and facing each other. A flat rectangular poly(tetrafluoroethylene) block about 10 x 20 x 5 mm. is placed between and about 1 cm. from one end of the plates and acts as an insulating separator. This electrode "sandwich" is fastened at the position of the poly(tetrafluoroethylene) block to form a rigid assembly with the electrode faces spaced 5 mm. apart. The electrode assembly is suspended in the dispersion with the separator above the surface of the liquid. Electrical connections are made to the electrodes above the liquid surface, and 100 volts D.C. is applied across the electrodes for 2 minutes. Silver bromide is deposited on the cathode to produce a composite photographic element. After drying, the photographic element so produced is exposed on a wedge spectrograph developed in a developing composition having the formula:

N-methyl-p-aminophenol	g--	2.0
Sodium sulfite (desiccated)	g--	90.0
Hydroquinone	g--	8.0
Sodium carbonate (monohydrate)	g--	52.5
Potassium bromide	g--	5.0
Water to make 1000 cc.		

and fixed in a fixing bath having the formula:

Sodium thiosulfate	g--	240
Sodium sulfite (desiccated)	g--	15
Acetic acid (28% aqueous)	cc--	48
Boric acid (crystals)	g--	7.5
Potassium alum	g--	15
Water to make 1000 cc.		

to yield a negative photographic silver image corresponding to the exposure scale.

EXAMPLE 2

An aqueous silver bromide precipitate is prepared by slowly pouring 500 ml. of hot 1.000 N silver nitrate solution into 500 ml. of hot 1.002 N KBr solution with vigorous stirring. After cooling, the supernatant solution is decanted and the precipitate is washed three times with 10^{-3} molar potassium bromide solution. The precipitate is treated with an excess of a dilute solution of 1,1'-diethyl-2,2'-cyanine bromide spectral sensitizing dye. The solids are allowed to settle and the dye solution is decanted. The solids are washed three times in a 10^{-3} molar potassium bromide solution. About 10 g. of the solids are dispersed in about 100 ml. distilled water. Two 1" x 3" NESAs (trademark of Pittsburgh Plate Glass Co.) transparent tin oxide coated glass electrodes and a 1 cm. x 1 cm. x 1" poly(tetrafluoroethylene) insulating separator are used to prepare an electrode sandwich similar to that described in Example 1 with a separation of 1 cm. between the conducting surfaces. The electrode assembly is suspended in the dispersion with the separator above the surface of the liquid. Electrical connections are made to the electrodes above the liquid surface; 10 volts D.C. is applied across the electrodes for 1 minute. Spectrally sensitized silver bromide is deposited on the cathode to produce a composite photographic element. Employing the exposure and processing procedures of Example 1, a similar photographic image is prepared.

EXAMPLE 3

A photographic element is prepared as in Example 1 except that the silver bromide dispersion is treated with an enzyme to effect removal of gelatin from the silver bromide crystals. The enzyme hydrolysis is according to the method of Weiss, Ericson and Herz, Journal of Colloid and Interface Science, 23, p. 277 (1967) and the electrodes are poly(ethylene terephthalate) having a titanium-gold conductive coating on one surface. Coating, exposure and processing are as in Example 1 and similar results are obtained.

EXAMPLE 4

An aqueous dispersion is prepared as in Example 1 ex-

10

cept that the AgBr is replaced by a silver dye complex prepared by reacting equimolar portions of .1 molar silver nitrate and a 1% methanolic solution of the merocyanine sensitizing dye, 3-carboxymethyl-5-[(3-methyl-2-thiazolylidene)ethylidene]rhodanine. The dispersion is centrifuged, decanted, washed and finally dispersed in nitromethane, all of which operations are performed as described in Example 1. Dilution and coating of the final dispersion are also accomplished, as in Example 1, utilizing a like support material. After drying the prepared photographic element having a silver-dye complex as the photosensitive species, the composite element is exposed on a wedge spectrograph and physically developed by immersion for two minutes in a physical developer solution having the formula:

(A)

Water	cc--	800
Sodium sulfite	g--	20
Sodium isoascorbate	g--	26
Sodium carbonate (monohydrate)	g--	50
Octylphenoxyethoxy ethyldimethyl - p - chlorobenzyl ammonium chloride (1% in H ₂ O)	cc--	22
Water to 1 liter.		
pH—11.0.		

(B)

Water	cc--	800
Sodium thiosulfate .5H ₂ O	g--	30
Silver chloride	moles--	5×10^{-2}
Water to 960 cc.		
5-methylbenzotriazole (1% in dil. KOH)	cc--	40

wherein parts A and B are mixed just prior to use. For making the silver chloride used in part B, 42.4 g. of silver nitrate are dissolved in 900 cc. of water, and 42.4 g. of potassium chloride is dissolved in a second 900 cc. of water. Then, 90 cc. of each solution are mixed in 6 ounce bottles which are allowed to stand overnight, after which time the liquid is poured off. The contents of two such bottles is required to make the 5×10^{-2} moles, since each contains 2.5×10^{-2} moles of silver chloride. After development, a dense silver image is present in the exposed areas.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. An electrophoretic coating process for preparing a photographic element comprising an electrically-conducting support having thereon a sensitive layer comprising radiation-sensitive silver salt crystals, said process comprising:

(A) dispersing said silver salt crystals in a liquid medium,

(B) immersing a portion of each of a pair of electrodes in said silver salt dispersion with one of the electrodes being located in a spaced relationship with the remaining electrode, and

(C) applying a D.C. potential across said pair of electrodes, whereupon dispersed silver salt is deposited upon an electrode of said electrode pair, which electrode is the support for said photographic element.

2. A process as described in claim 1 wherein said electrodes are immersed in a parallel spaced relationship.

3. A process as described in claim 1 wherein said silver salt crystals comprise silver halide crystals selected from the group consisting of silver bromide, silver chloride, silver iodide and mixtures thereof.

4. A process as described in claim 3 wherein said silver halide crystals are spectrally sensitized with a silver halide sensitizing dye.

5. A process as described in claim 1 wherein said silver salt is a silver-sensitizing dye complex.

11

6. A process as described in claim 1 wherein said silver halide crystals are codispersed with a hydrophilic colloid binder material.

7. A process as described in claim 1 wherein said electrodes are selected from the group consisting of metal plates, electrically insulating plates having a conducting layer thereon and resinous, flexible photographic film base having a conducting layer thereon. 5

8. An electrophoretic coating process for preparing a photographic element comprising an electrically-conducting support having coated thereon a light-sensitive layer comprising silver halide, said process comprising: 10

(A) dispersing photosensitive silver halide crystals in a liquid medium, 15

(B) positioning a portion of each of a pair of electrodes, said electrodes comprising a glass plate having coated thereon an electrically-conducting chromium layer in said silver halide dispersion with one of the electrodes being located in a parallel spaced rela- 20

12

tionship with the remaining electrode and with said electrically-conducting chromium layers facing each other,

(C) applying a D.C. potential of about 1000 volts across said pair of electrodes,

whereupon photosensitive silver halide is deposited on an electrode of said electrode pair, which electrode is the support for the photographic element.

References Cited**UNITED STATES PATENTS**

3,402,111	9/1968	Ville	-----	204—181
3,384,566	5/1968	Clark	-----	204—181
3,462,286	8/1969	De Geest et al.	-----	204—181

HOWARD S. WILLIAMS, Primary Examiner

U.S. Cl. X.R.

96—94 BF

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,684,675 Dated August 15, 1972

Inventor(s) Warren J. Miller

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

Column 3, line 36, " $\text{C-SO}_3\text{Na}_5$ " should read

--- $\text{C-SO}_3\text{Na}$, ---;

Column 3, line 55, "3-3-carboxymethyl" should read

---3-carboxymethyl---

Signed and sealed this 23rd day of January 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents