

1

3,396,028

SILVER HALIDE EMULSIONS CONTAINING HYDROXY CARBOXYLIC ACID DERIVATIVES AS FOG INHIBITORS

Wilbert J. Humphlett, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed Nov. 25, 1964, Ser. No. 413,962
19 Claims. (Cl. 96—109)

ABSTRACT OF THE DISCLOSURE

Photographic silver halide emulsions containing derivatives of hydroxy carboxylic acids as antifoggants and elements comprising such emulsions are disclosed.

This invention relates to stabilized photographic compositions, and more particularly, to photographic silver halide emulsions containing novel fog-inhibiting agents.

It is well known that photographic emulsions on storage tend to lose sensitivity and to become spontaneously developable without exposure to light. There is normally a detectable amount of the silver salt reduced during development in the areas where no exposure was given, this commonly being called "fog," and sometimes "chemical fog" where it is necessary to distinguish between it and the effects of accidental exposure to radiation. In this invention, I am concerned with the former, namely, chemical fog. Also, the present invention should be distinguished from methods for preventing "color fog" or stain resulting in color photography from oxidized color developer at places where silver halide is not reduced.

Fog as contemplated herein depends both on the emulsion and the conditions of development. For a given emulsion, fog increases with the degree of development. With constant development conditions, fog tends to increase with time, temperature and relative humidity of storage conditions. It is common practice to make accelerated tests of the stability of photographic emulsions by storage at increased temperature or humidity, or both. It is of course desirable to have emulsions as stable as possible under the conditions of high temperature and humidity which may occur in tropical climates, for example. Fog usually appears over the whole area of the sensitive coating, but when severe, it frequently is nonuniform. Fog may also be caused by exposure to chemicals, for example, hydrogen sulfide and other reactive sulfur compounds, hydrogen peroxide vapor, and strong reducing materials. While antifoggants and stabilizers may protect, to some extent, against such effects, it is normally understood that an antifoggant protects against spontaneous growth of fog during prolonged storage or storage at high temperatures and humidities, or during development to maximum contrast and speed, or both.

It is hence an object of this invention to inhibit fog formation in photographic silver halide emulsions with novel emulsion addenda.

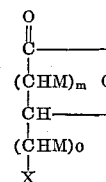
It is also an object of this invention to provide new photographic silver halide emulsions containing antifoggant addenda that do not cause objectionable desensitization of the emulsion.

These and other objects of the invention are accomplished by incorporating into photographic silver halide

2

emulsions antifoggant amounts of derivatives of hydroxy carboxylic acids having Formulas I and II,

I.

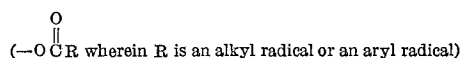


and

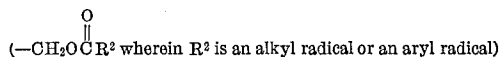
II.



wherein: M and Z are each hydroxy radicals or acyloxy radicals



X is a hydrogen atom, an acyloxymethyl radical



or a carbinol radical ($-\text{CH}_2\text{OH}$); Y is a carboxy radical



a carbamyl radical



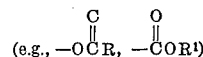
or a radical having the formula



wherein R¹ is an alkyl radical (more generally having 1 to 2 carbons, particularly when Z is a hydroxyl radical); A is a carbinol radical, a radical having the formula

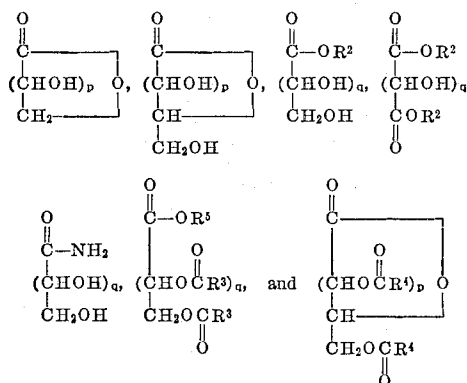


as described for Y, a carboxy radical, an acyloxymethyl radical or a carbamyl radical; m is an integer of 2 to 3; n is an integer of 1 to 5; and o is an integer of 0 to 2. The subject addenda contain at least one carbamyl or ester moiety including γ or δ lactone or inner ester groups (e.g., Formula I) as well as the more conventional ester groups described above



Hence, at least one of A, Y and Z of Formula II forms a carbamyl or an ester radical. Typical useful antifoggant

addenda can be represented by the following more sub-generic formulas:



wherein: R^2 is an alkyl radical having 1 to 2 carbon atoms; R^3 and R^4 are each an alkyl radical which more generally has 1 to 8 carbon atoms or a phenyl radical, including substituted phenyl radicals; R^5 is an alkyl radical which more generally has 1 to 8 carbon atoms or a hydrogen atom; p is an integer of 2 to 3; and q is an integer of 1 to 5. Other subgeneric formulas defining antifoggant addenda of the invention included within generic Formulas I and II can be formulated. The alkyl substituents described above suitably have 1 to 20 carbon atoms, and preferably 1 to 8 carbon atoms, including methyl, ethyl, isopropyl, butyl, heptyl, octyl, decyl, octadecyl, eicosyl and the like. The aryl substituents described above include such radicals as phenyl, tolyl, naphthyl and the like, phenyl being preferred.

As described above, a wide variety of amide or ester-hydroxy carboxylic acid derivatives can be utilized as antifoggant addenda for photographic silver halide emulsions. Such compounds can be prepared by conventional amidation and esterification techniques with such saturated, aldehyde radical-free, hydroxy carboxylic acids as glyceric, erythronic, arabonic, lyxonic, ribonic, xylonic, gluconic, galactonic, mannonic, gulonic, tartaric, gluculoheptonic and the like hydroxy carboxylic acids.

Literature references describing the preparation of typical antifoggant addenda of the invention include:

- (a) J. Am. Chem. Soc., 37, 345 (1915)
- (b) J. Am. Chem. Soc., 55, 2512 (1933)
- (c) J. Am. Chem. Soc., 62, 1074 (1940)
- (d) J. Am. Chem. Soc., 69, 915 (1947)
- (e) J. Org. Chem., 18, 952 (1953)
- (f) J. Am. Chem. Soc., 78, 2825 (1956)
- (g) Helv. Chim., Acta, 34, 2343
- (h) J. Am. Pharm. Assoc., 28, 364 (1949)
- (i) U.S. Patent 2,380,444

Other references can be found in the literature describing the preparation of the present feature addenda.

The addenda of the invention described above can be added to the photographic silver halide emulsions for purposes of increasing the stability thereof. More specifically the subject addenda serve as emulsion antifoggants. Many antifoggant addenda cause substantial desensitizations or loss in speed of the emulsion when employed therein antifoggant amounts. However, with the subject addenda there is no objectionable loss of speed imparted to emulsions.

The particular quantity of the present stabilizers used in a given emulsion can vary, depending upon the effects desired, degree of ripening, silver content of the emulsion, etc. I have found that generally from about 5 to 100 grams of the feature addenda per mole of silver halide are quite adequate to accomplish the desired stabilization, with about 10 to 50 grams of the addenda per mole of silver halide being preferred. Exposure of the treated emulsion in conventional photographic testing apparatus, such as an intensity scale sensitometer, will re-

veal the most advantageous concentrations for the present stabilizers in that particular emulsion. Such techniques are well understood by those skilled in the art.

The addenda of the invention can be added to photographic emulsions using any of the well-known techniques in emulsion making. For example, they can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a dispersion similar to the technique used to incorporate certain types of color-forming compounds (couplers) in a photographic emulsion. Techniques of this type are described in Jelley et al., U.S. Patent 2,322,027, issued June 15, 1943, and Fierke et al., U.S. Patent 2,801,171, issued July 30, 1957. The solvent should be selected so that it has no harmful effect upon the emulsion in accordance with usual practice, and generally solvents or diluents which are miscible with water are to be preferred.

In addition to the subject antifoggant addenda, the photographic emulsions of the invention can contain the usual well-known emulsion addenda such as spectral sensitizers, speed increasing materials (e.g. polyalkylene glycols, cationic compounds, thioethers, etc.), coating aids, gelatin hardeners, plasticizers and the like.

The stabilizer addenda of the invention can be used in various kinds of photographic emulsions. They can be used with silver halide emulsions chemically sensitized with compounds of the sulfur group, with noble metal salts such as gold salts, reducing agents or combinations of these. In addition to being useful in orthochromatic, panchromatic, and infrared sensitive emulsions, they are also useful in X-ray and other nonspectrally sensitized emulsions. They can be added to the emulsion before or after any spectral sensitizing dyes which may be used. Various silver salts can be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromiodide. The subject addenda can be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, dye developer systems and dye bleach systems.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there can be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound, although gelatin is preferred. Mixtures can be used (e.g. gelatin+polyacrylamide).

The above-described emulsions of the invention can be coated on a wide variety of supports in accordance with usual practice. Typical supports for photographic elements of the invention include cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film and related films or resinous materials, as well as glass, paper, polyethylene coated paper, metals, wood and others.

The invention is further illustrated by the following examples.

Example 1

A high-speed sulfur-gold sensitized gelatin silver bromide emulsion was prepared, various antifoggant addenda of the invention were added to separate portions thereof, and the resulting compositions were coated on cellulose acetate film supports at coverages of 459 mg. of silver per square foot and 1040 mg. of gelatin per square foot. Similar photographic elements were prepared without the feature antifoggant addenda for purposes of comparison. Samples of the prepared photographic elements were incubated for 7 or 14 days at 120° F. and 50% relative humidity, exposed in the form of film strips in an intensity scale sensitometer (Eastman IB sensitometer), developed for 5 minutes at 68° F., and then fixed, washed and dried in the usual manner. Test samples were also exposed in

the sensitometer directly after coating for purposes of comparison. The developer had the following formula:

TABLE B—Continued

DEVELOPER	Grams
N-methyl-p-aminophenolsulfate -----	2.5
Hydroquinone -----	2.5
Sodium sulfite (anhydrous) -----	30.0
Sodium metaborate octahydrate -----	10.0
Potassium bromide -----	0.5
Water to make one liter.	

The results of the sensitometric tests are summarized by the data set out in Table A below with respect to relative speed, gamma (γ) and fog. In Table A below, the speeds indicated are a function of the exposure necessary to give a density of 0.2 above background fog, the initial control speed being taken as 100 in each case; and the concentrations of addenda are indicated as grams of addenda per mole of silver halide.

Feature addenda:	Conc. of feature addenda (g./mole AgX)
Ethyl L-arabonate -----	5
Ethyl D,L-arabonate -----	45
Methyl D-arabonate tetraacetate -----	45
n-Propyl D-arabonate tetraacetate -----	45
Isopropyl D-arabonate tetraacetate -----	15
2,3,4,6-tetraacetyl-D-gluconic acid mono-hydrate -----	30
D-galactono- γ -lactone -----	45
D-galactonamide -----	30
Methyl D-galactonate -----	45
Ethyl D-mannonate -----	45
D-lyxono- γ -lactone -----	6
D-lyxonamide -----	6
L-erythrono- γ -lactone -----	45
Methyl L-arabonate -----	9, 25

TABLE A

Feature Addenda	Conc. of Feature Addenda	Fresh Test			7 Days, 120° F., 50% R.H.			14 Days, 120° F., 50% R.H.		
		Rel. Speed	γ	Fog	Rel. Speed	γ	Fog	Rel. Speed	γ	Fog
Control.....	0	100	1.23	.10	-----	-----	-----	-----	-----	>1.00
Diethyl imucate.....	9	100	1.30	.10	-----	-----	-----	49	.98	.47
Do.....	45	100	1.37	.09	-----	-----	-----	54	1.08	.22
Control.....	0	100	1.35	.13	-----	-----	-----	31	.82	.69
Methyl D-arabonate.....	9	95	1.35	.14	-----	-----	-----	53	1.05	.31
Do.....	45	91	1.45	.10	-----	-----	-----	68	1.15	.10
Control.....	0	100	1.15	.12	-----	-----	-----	24	.65	1.03
Ethyl D-arabonate.....	10.35	102	1.00	.10	-----	-----	-----	52	.93	.45
Do.....	45	94	1.05	.07	-----	-----	-----	89	1.15	.10
Control.....	0	100	1.25	.16	-----	-----	-----	19	.60	1.09
Methyl L-arabonate tetraacetate.....	30	105	1.30	.09	-----	-----	-----	95	1.20	.15
Control.....	0	100	1.35	.14	89	1.13	.25	-----	-----	-----
D-Arabono- γ -lactone.....	45	94	1.27	.08	96	1.23	.06	-----	-----	-----
Control.....	0	100	1.28	.15	69	1.00	.30	-----	-----	-----
Isobutyl D-arabonate tetraacetate.....	45	102	1.33	.13	80	1.13	.20	-----	-----	-----
Methyl(tetraacetyl-D-arabonyl)glycolate.....	45	100	1.27	.12	78	1.10	.20	-----	-----	-----
Control.....	0	100	1.60	.16	87	1.13	.26	-----	-----	-----
D-Gluco-D-gulo-heptono- γ -lactone.....	45	94	1.45	.10	73	1.23	.11	-----	-----	-----
D-Gluco-D-gulo-heptonoamide.....	45	100	1.55	.12	82	1.22	.11	-----	-----	-----
Control.....	0	100	1.60	.16	87	1.13	.26	-----	-----	-----
Methyl D,L-glycerate.....	45	89	1.55	.11	74	1.20	.12	-----	-----	-----
Control.....	0	100	1.35	.14	89	1.13	.25	-----	-----	-----
Dimethyl D-tartrate.....	45	94	1.28	.07	94	1.13	.10	-----	-----	-----
Control.....	0	100	1.35	.14	89	1.13	.25	16	.82	.93
D-Glucono- δ -lactone.....	45	83	1.35	.07	89	1.30	.05	62	1.30	.08
Control.....	0	100	1.60	.16	87	1.13	.26	30	.90	.82
D-Gluconamide.....	45	100	1.60	.12	78	1.28	.12	73	1.12	.12
Control.....	0	100	1.23	.15	82	1.04	.26	50	.81	.62
D-Gluco-D-gulo-heptonic acid hexaacetate monohydrate.....	18	83	1.27	.10	65	1.03	.10	60	.97	.10
L-Erythronic acid tribenzoate.....	18	60	1.13	.12	53	1.02	.13	52	.95	.15
Control.....	0	100	1.33	.17	74	1.14	.24	29	.73	.83
D-Galactonic acid pentaacetate.....	28.5	85	1.43	.14	74	1.30	.12	60	1.12	.11

Data similar to that illustrated in Table A above was also obtained with hydroxy carboxylic acid derivatives of the invention listed in Table B below when incorporated in the silver halide emulsion described above, and thereafter incubated, exposed and processed as described above. Substantially reduced fog levels without objectionable reduction in speed were obtained in each instance after the incubation period as compared to the same emulsion containing no feature hydroxy carboxylic acid derivative.

TABLE B

Feature addenda:	Conc. of feature addenda (g./mole AgX)
L-arabono- γ -lactone -----	45
D,L-arabono- γ -lactone -----	45
D-arabonamide -----	45
Methyl D,L-arabonate -----	45

Methyl(methyl α -D-galactopyranoside)uronate monohydrate -----	45
D-manno- γ -lactone -----	10.6
D-mannonamide -----	13.95
D-glucono- γ -lactone -----	45
D-ribonic acid tetraacetate -----	26.55
L-erythronamide -----	45
D-ribono- γ -lactone -----	45

Example 2

For purposes of comparison, several compounds closely related to the antifoggant addenda of the invention were incorporated into the high-speed gelatino silver halide emulsion described in Example 1, and thereafter incu-

bated, exposed and processed as described in Example 1. The results are summarized by the data in Table C below.

invention as described hereinabove and as defined in the appended claims.

TABLE C

Feature Addenda	Conc. of Feature Addenda	Fresh Test			7 Days, 120° F., 50% R.H.			14 Days, 120° F., 50% R.H.		
		Rel. Speed	γ	Fog	Rel. Speed	γ	Fog	Rel. Speed	γ	Fog
Control.....	0	100	1.28	.13				18	.60	1.00
Sucrose.....	45	105	1.45	.10						>1.00
Glucuronic acid.....	45	97	1.33	.12						>1.00
Control.....	0	100	1.20	.12				17.2	.60	1.12
D-Glucose.....	45	107	1.33	.07						>1.00
Control.....	0	100	1.15	.12				24	.65	1.03
D-Arabinic acid.....	45	107	1.12	.10						>1.00
D-Arabinic acid potassium salt.....	45	97	1.10	.10						>1.00
Control.....	0	100	1.60	.16	87	1.13	.26			
Methyl α -D-galactopyranuronate.....	42.75	95	1.42	.12			>1.00			
Methyl 2-ketogulonate.....	15	91	1.50	.20			>1.00			
Control.....	0	100	1.60	.16	87	1.13	.26			
Methyl glucolate.....	45	100	1.52	.13	74	1.10	.26			
Control.....	0	100	1.28	.15	69	1.00	.30			
Ethylene bis(D-arabonate tetraacetate).....	45	68	.92	.10	68	1.00	.29			

Examples 3 and 4 below describe the preparation of two typical addenda of the invention. Other addenda of the invention can be prepared by methods described in the literature set out above.

Example 3.—(D-arabono- γ -lactone)

Twenty-five g. (0.122 mole) of potassium D-arabonate was suspended in 75 ml. of n-butyl alcohol in a 200 ml. Erlenmeyer flask. Gaseous, dry hydrogen chloride was bubbled into the mixture, with cooling in an ice-water bath since considerable heat was generated. After 10 minutes, introduction of hydrogen chloride was stopped, and the precipitate of potassium chloride was separated by suction filtration. The precipitate was rinsed with 25 ml. of hot n-butyl alcohol. The combined filtrates were concentrated in vacuo on a steam bath leaving a residue of a sirup which crystallized quickly on cooling. After standing overnight, the crude product was collected, amounting to 18 g. or 100% of the theoretical yield and melting at 96 to 98° C. The crude product was recrystallized from a mixture of acetone and ether, M.P. 98° C.

Example 4.—(Isobutyl D-arabonate tetraacetate)

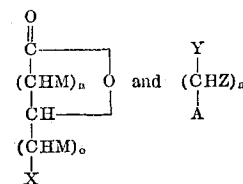
To a solution of 4.15 g. (0.0118 mole) of D-arabonyl chloride tetraacetate in 50 ml. of chloroform was added 4 g. of isobutyl alcohol and 4 g. of pyridine. The reaction became warm. After standing overnight, the chloroform solution was extracted successively with water, dilute hydrochloric acid, dilute sodium bicarbonate solution and water. The aqueous extracts were each extracted with chloroform. The combined chloroform portions were dried over anhydrous sodium sulfate, filtered and the solvent removed by boiling. The last of the solvent was removed in vacuo, leaving a sirup. A few crystals appeared on the edge of the sirup after standing for several days. Scratching with a glass stirring rod then hastened crystallization of the waxy solid. After standing overnight in a refrigerator, the hardened crude product, melting at 41° C., amounted to 4.41 g. or 96% of the theoretical yield. Recrystallization three times from a mixture of ether and low boiling ligroin did not alter the melting point.

The invention thus provides new and useful photographic silver halide emulsions, and which emulsions have high resistance to the formation of fog.

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

I claim:

1. A photographic silver halide emulsion containing a hydroxy carboxylic acid derivative antifoggant having a formula selected from the group consisting of



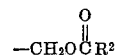
wherein.

(1) M and Z are each selected from the group consisting of a hydroxy radical and an acyloxy radical having the formula



wherein R is selected from the group consisting of an alkyl radical and an aryl radical;

(2) X is selected from the group consisting of a hydrogen atom, a carbinol radical, a radical having the formula



wherein R² is selected from the group consisting of an alkyl radical and an aryl radical;

(3) Y is selected from the group consisting of a carboxy radical, a carbamyl radical and a radical having the formula

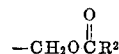


wherein R¹ is an alkyl radical;

(4) A is selected from the group consisting of a carbinol radical, a carbamyl radical, a carboxy radical, a radical having the formula



wherein R¹ is an alkyl radical and a radical having the formula



wherein R² is selected from the group consisting of an alkyl radical and an aryl radical;

(5) m is an integer of 2 to 3;

(6) n is an integer of 1 to 5; and

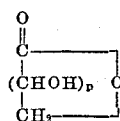
(7) o is an integer of 0 to 2;

except that at least one of A, Y and Z forms a radical

9

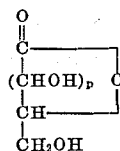
selected from the group consisting of a carbamyl radical and an ester radical.

2. A photographic silver halide emulsion containing a hydroxy carboxylic acid derivative antifoggant having the formula



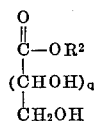
wherein p is an integer of 2 to 3.

3. A photographic silver halide emulsion containing a hydroxy carboxylic acid derivative antifoggant having the formula



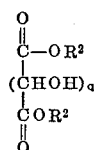
wherein p is an integer of 2 to 3.

4. A photographic silver halide emulsion containing a hydroxy carboxylic acid derivative antifoggant having the formula



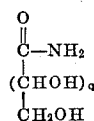
wherein q is an integer of 1 to 5 and R^2 is an alkyl radical having 1 to 2 carbon atoms.

5. A photographic silver halide emulsion containing a hydroxy carboxylic acid derivative antifoggant having the formula



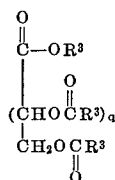
wherein q is an integer of 1 to 5.

6. A photographic silver halide emulsion containing a hydroxy carboxylic acid derivative antifoggant having the formula



wherein q is an integer of 1 to 5.

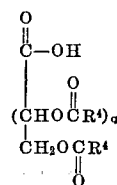
7. A photographic silver halide emulsion containing a hydroxy carboxylic acid derivative antifoggant having the formula



wherein q is an integer of 1 to 5 and R^3 is an alkyl radical having 1 to 8 carbon atoms.

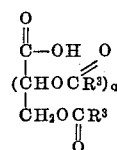
10

8. A photographic silver halide emulsion containing a hydroxy carboxylic acid derivative antifoggant having the formula



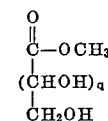
wherein q is an integer of 1 to 5 and R^4 is a phenyl radical.

9. A photographic silver halide emulsion containing a hydroxy carboxylic acid derivative antifoggant having the formula



wherein q is an integer of 1 to 5 and R^3 is an alkyl radical having 1 to 8 carbon atoms.

10. A photographic silver halide emulsion containing a hydroxy carboxylic acid derivative antifoggant having the formula



wherein q is an integer of 1 to 5.

11. A photographic silver halide emulsion as described in claim 1 wherein gelatin is used as the dispersing agent for the silver halide.

12. A photographic silver halide emulsion as described in claim 1 wherein the silver halide is silver bromiodide.

13. A photographic element comprising a photographic emulsion support having coated thereon a photographic silver halide emulsion as described in claim 1.

14. A photographic gelatino silver halide emulsion containing about 5 to 100 grams per mole of silver halide in said emulsion of methyl L-arabonate.

15. A photographic gelatino silver halide emulsion containing about 5 to 100 grams per mole of silver halide in said emulsion of methyl D-arabonate.

16. A photographic gelatino silver halide emulsion containing about 5 to 100 grams per mole of silver halide in said emulsion of ethyl D-arabonate.

17. A photographic gelatino silver halide emulsion containing about 5 to 100 grams per mole of silver halide in said emulsion of D-arabono- γ -lactone.

18. A photographic gelatino silver halide emulsion containing about 5 to 100 grams per mole of silver halide in said emulsion of D-arabonamide.

19. A photographic silver halide emulsion containing a hydroxy carboxylic acid derivative antifoggant selected from the group consisting of

- Diethyl mucate
- Methyl D-arabonate
- Ethyl D-arabonate
- Methyl L-arabonate tetra-acetate
- D-arabono- γ -lactone
- Isobutyl D-arabonate tetra-acetate
- Methyl (tetraacetyl-D-arabonyl)glycolate
- D-gluco-D-gulo-heptono- γ -lactone
- D-gluco-D-gulo-heptonoamide
- Methyl D,L-glycerate
- Dimethyl D-tartrate
- D-glucono δ -lactone
- D-gluconamide
- D-gluco-D-gulo-heptonic acid hexaacetate monohydrate

11

L-erythronic acid tribenzoate
 D-galactonic acid pentaacetate
 L-arabono- γ -lactone
 D,L-arabono- γ -lactone
 D-arabonamide
 Methyl D,L-arabonate
 Ethyl L-arabonate
 Ethyl D,L-arabonate
 Methyl D-arabonate tetraacetate
 n-Propyl D-arabonate tetraacetate
 Isopropyl D-arabonate tetraacetate
 2,3,4,6-tetraacetyl-D-gluconic acid monohydrate
 D-galactono- γ -lactone
 D-galactonamide
 Methyl D-galactonate
 Ethyl D-mannonate
 D-lyxono- γ -lactone
 D-lyxonamide
 L-erythrono- γ -lactone
 D-gluco-D-gulo-heptono- γ -lactone

12

D-gluco-D-gulo-heptonamide
 Methyl D,L-glycerate
 Methyl L-arabonate
 Methyl(methyl α -D-galactopyranoside)uronate
 5 monohydrate
 D-manno- γ -lactone
 D-mannonamide
 D-glucono- γ -lactone
 D-ribonic acid tetraacetate
 10 L-erythronamide and
 D-ribono- γ -lactone.

References Cited

UNITED STATES PATENTS

15 3,297,446 1/1967 Dunn ----- 96—107

NORMAN G. TORCHIN, *Primary Examiner.*

J. R. EVERETT, *Assistant Examiner.*

20

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

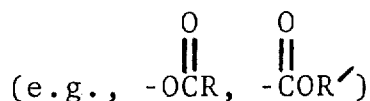
Patent No. 3,396,028

August 6, 1968

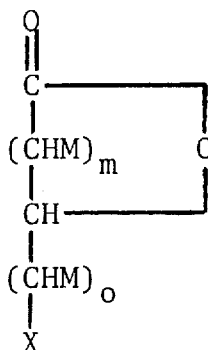
Wilbert J. Humphlett

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

Column 2, lines 59 and 60, the formula should appear as shown below:



Column 3, line 63, after "therein" insert -- in --. Column 4, line 52, "suports" should read -- supports --. Column 8, lines 28 to 35, the left-hand formula should appear as shown below:



Signed and sealed this 3rd day of February 1970.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents