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(12) **United States Patent**
Bolton(10) **Patent No.:** US 12,394,841 B2
(45) **Date of Patent:** *Aug. 19, 2025(54) **ZINC BATTERY ELECRTOLYTE ADDITIVE**(71) Applicant: **Onas Bolton**, Pepper Pike, OH (US)(72) Inventor: **Onas Bolton**, Pepper Pike, OH (US)(73) Assignee: **OCTET SCIENTIFIC, INC.**,
Cleveland, OH (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 665 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **17/746,432**(22) Filed: **May 17, 2022**(65) **Prior Publication Data**

US 2022/0278394 A1 Sep. 1, 2022

Related U.S. Application Data

(63) Continuation-in-part of application No. 16/752,170, filed on Jan. 24, 2020, now Pat. No. 11,424,484.

(60) Provisional application No. 62/796,296, filed on Jan. 24, 2019.

(51) **Int. Cl.****H01M 12/06** (2006.01)**H01M 4/24** (2006.01)**H01M 10/42** (2006.01)**H01M 12/02** (2006.01)(52) **U.S. Cl.**CPC **H01M 12/06** (2013.01); **H01M 4/244** (2013.01); **H01M 10/4235** (2013.01); **H01M 12/02** (2013.01); **H01M 2300/0014** (2013.01)(58) **Field of Classification Search**CPC .. H01M 4/244; H01M 12/06; H01M 10/4235;
H01M 2300/0014; H01M 12/02

See application file for complete search history.

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Primary Examiner — Laura Weiner*(74) Attorney, Agent, or Firm* — Dominic Frisina;
Buckingham, Doolittle & Burroughs, LLC(57) **ABSTRACT**

An electrolyte additive is provided. The additive is a quaternary ammonium or phosphonium salt effective to suppress hydrogen evolution and metal dendrite formation during operation of a zinc electrochemical cell such as a zinc-air battery. A zinc battery cell is also provided, which contains an effective amount of the electrolyte additive.

3 Claims, 32 Drawing Sheets

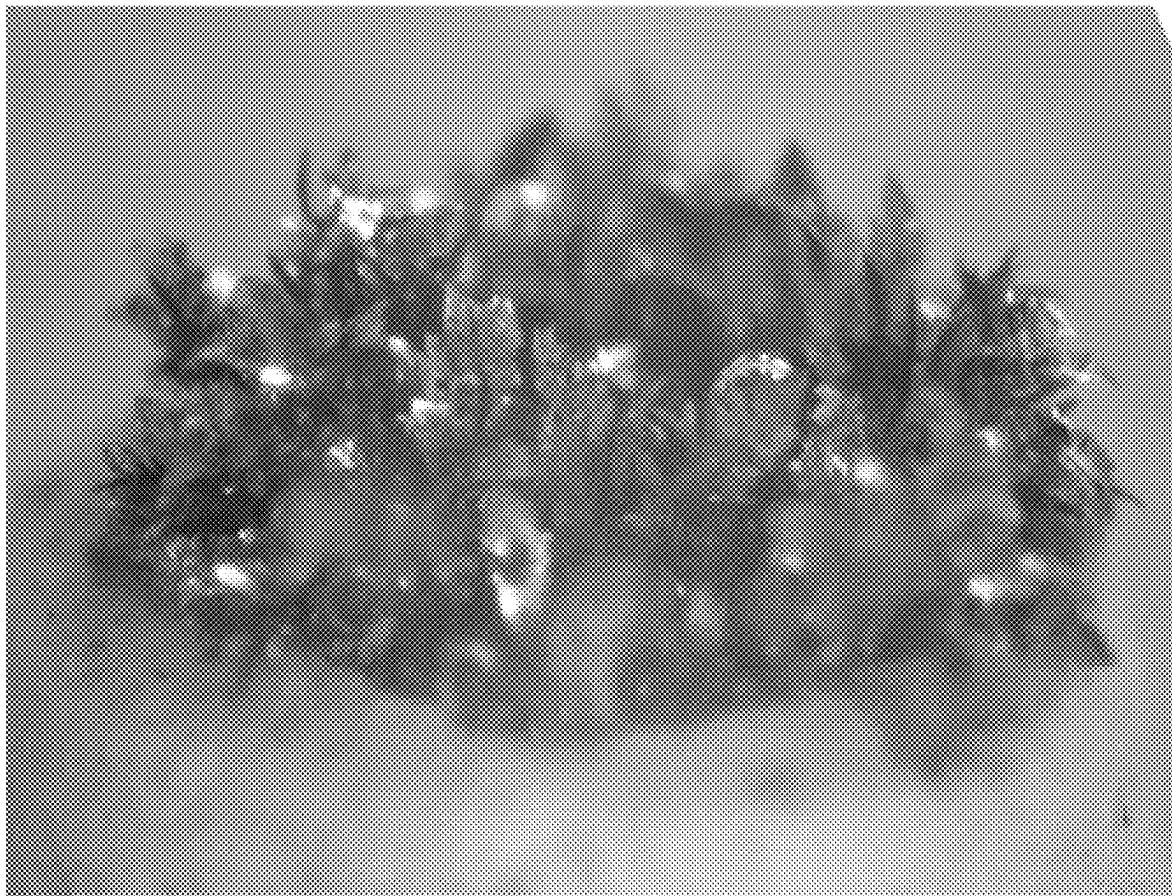


FIG. 1

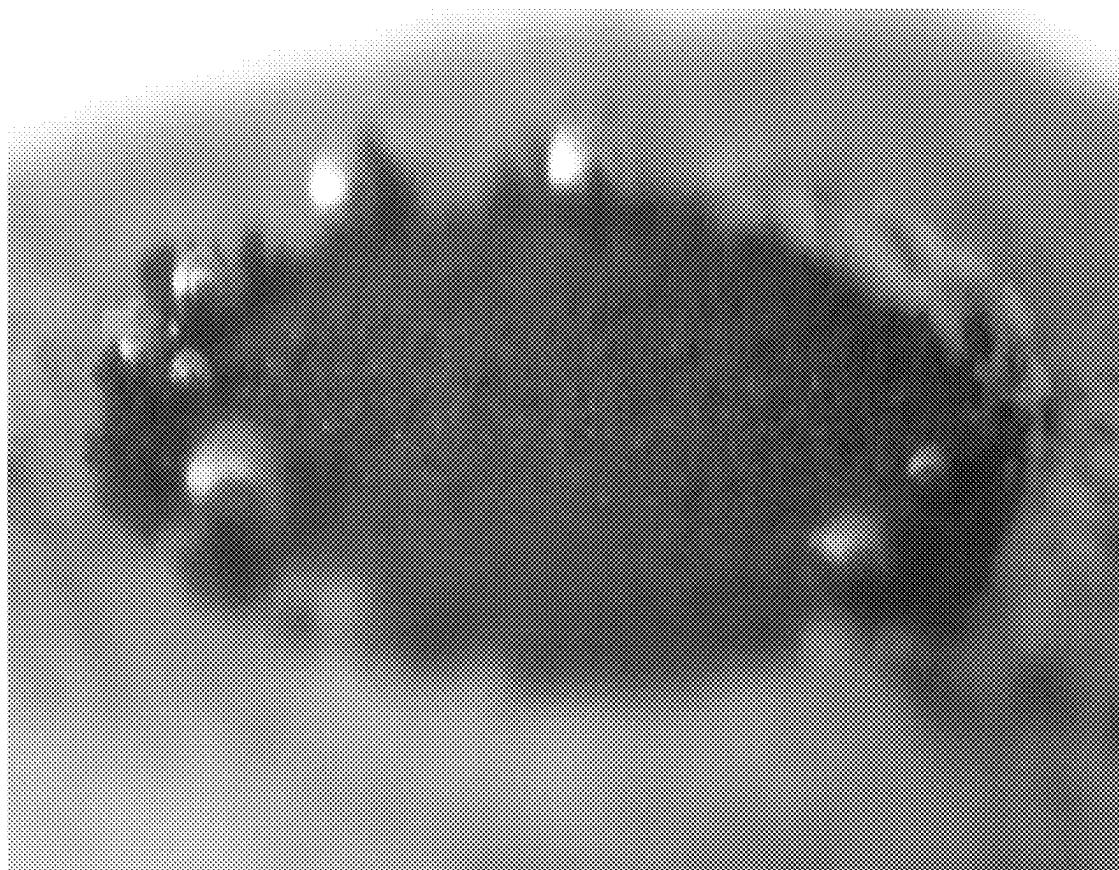


FIG. 2

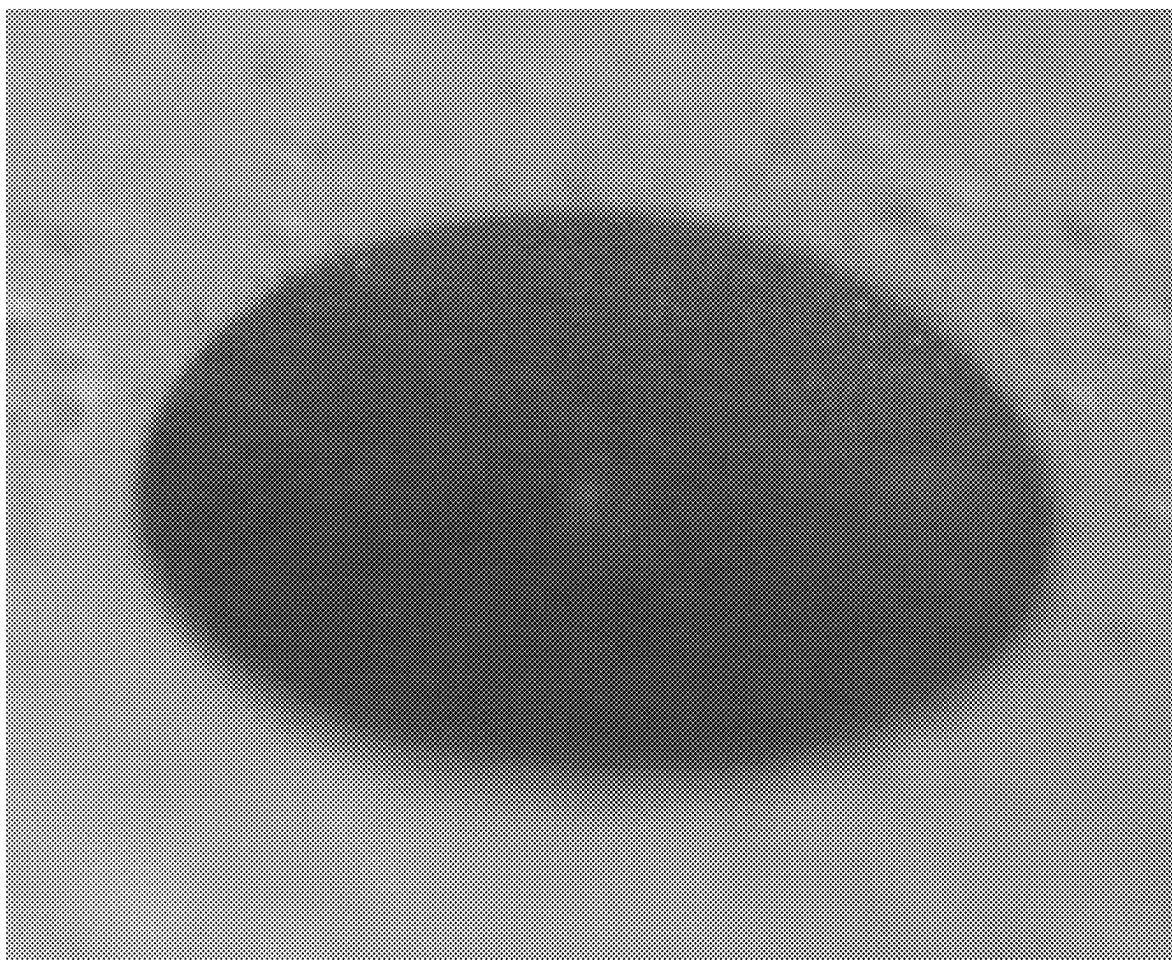


FIG. 3

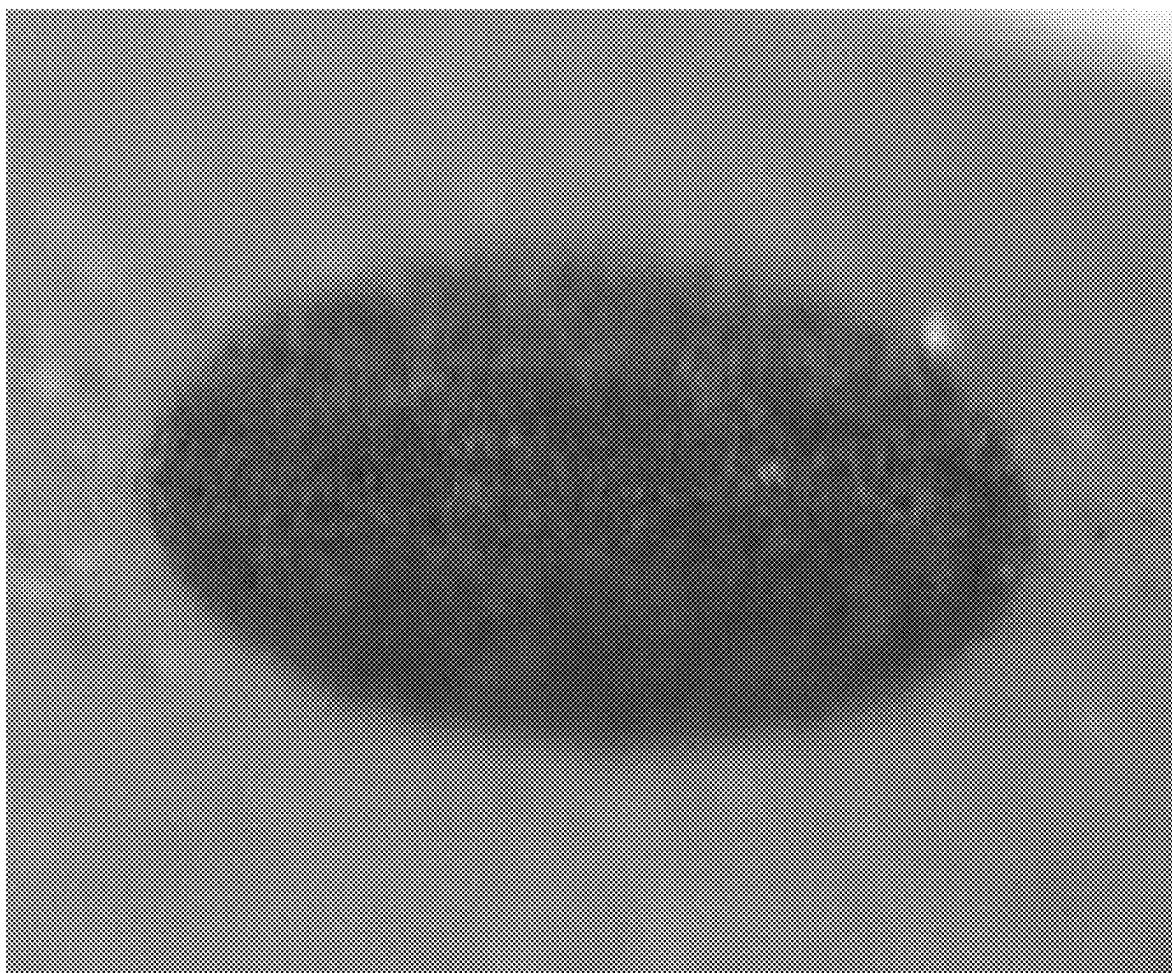


FIG. 4

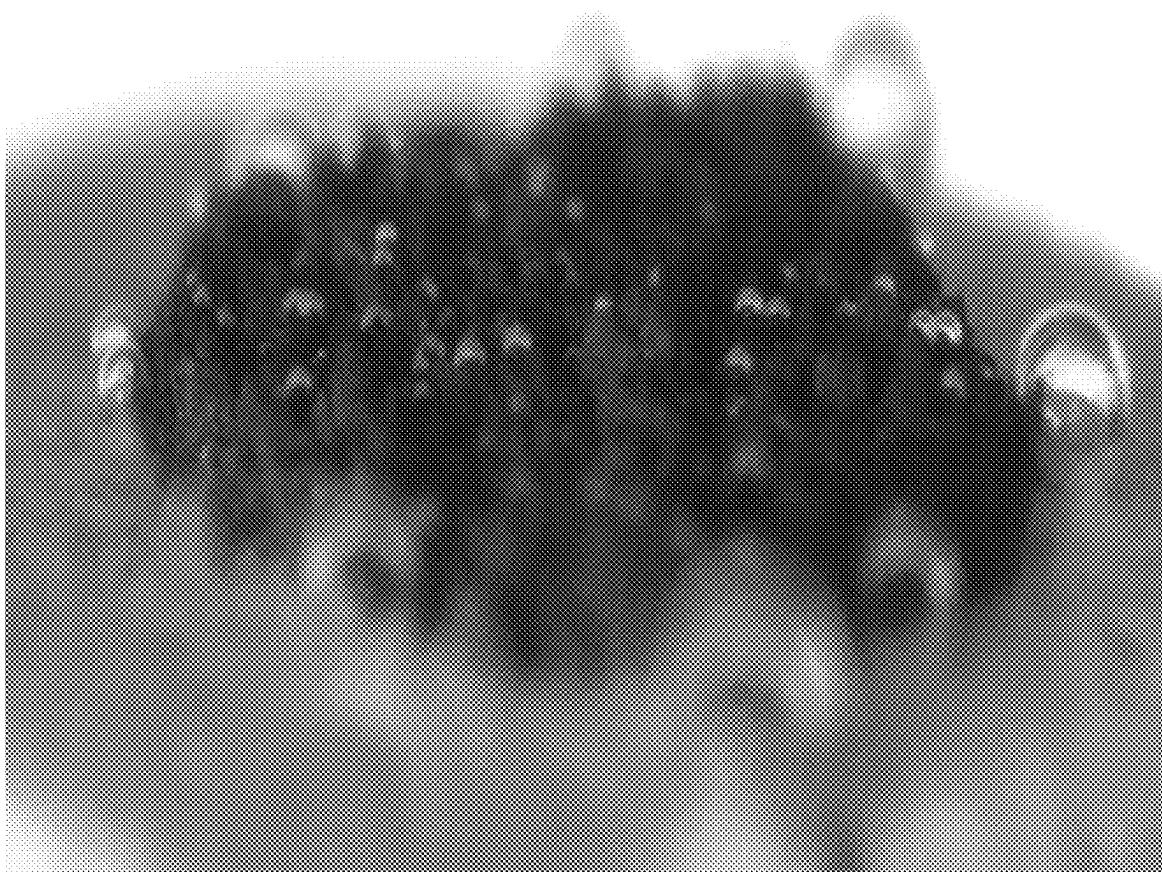


FIG. 5

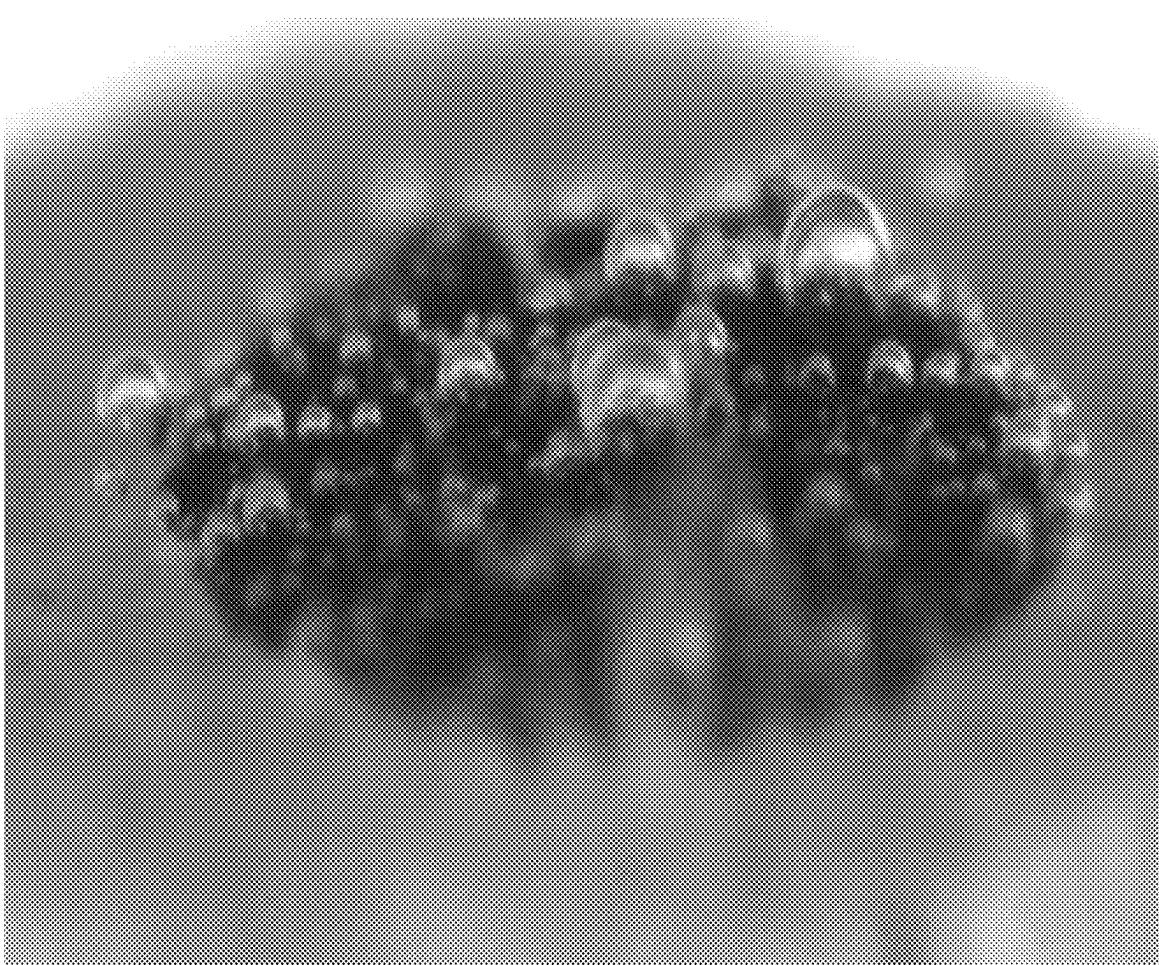


FIG. 6

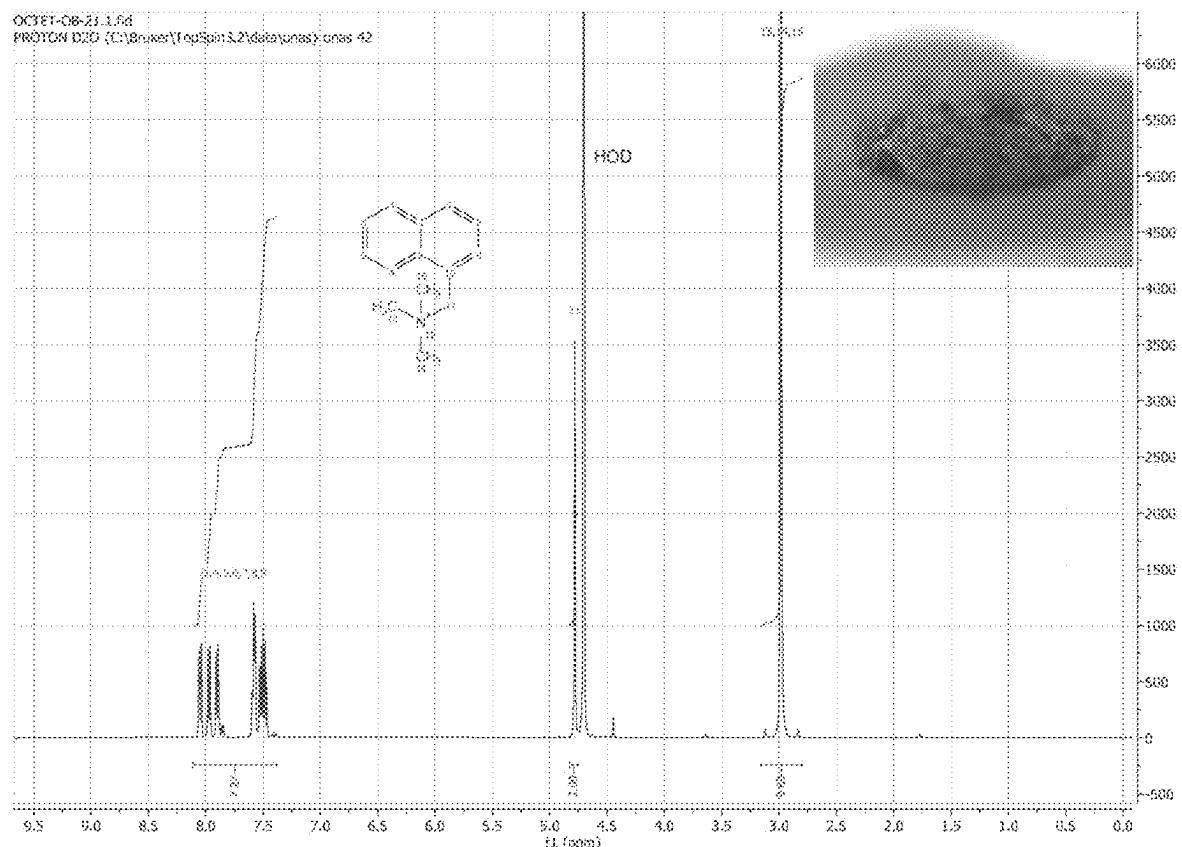


FIG. 7

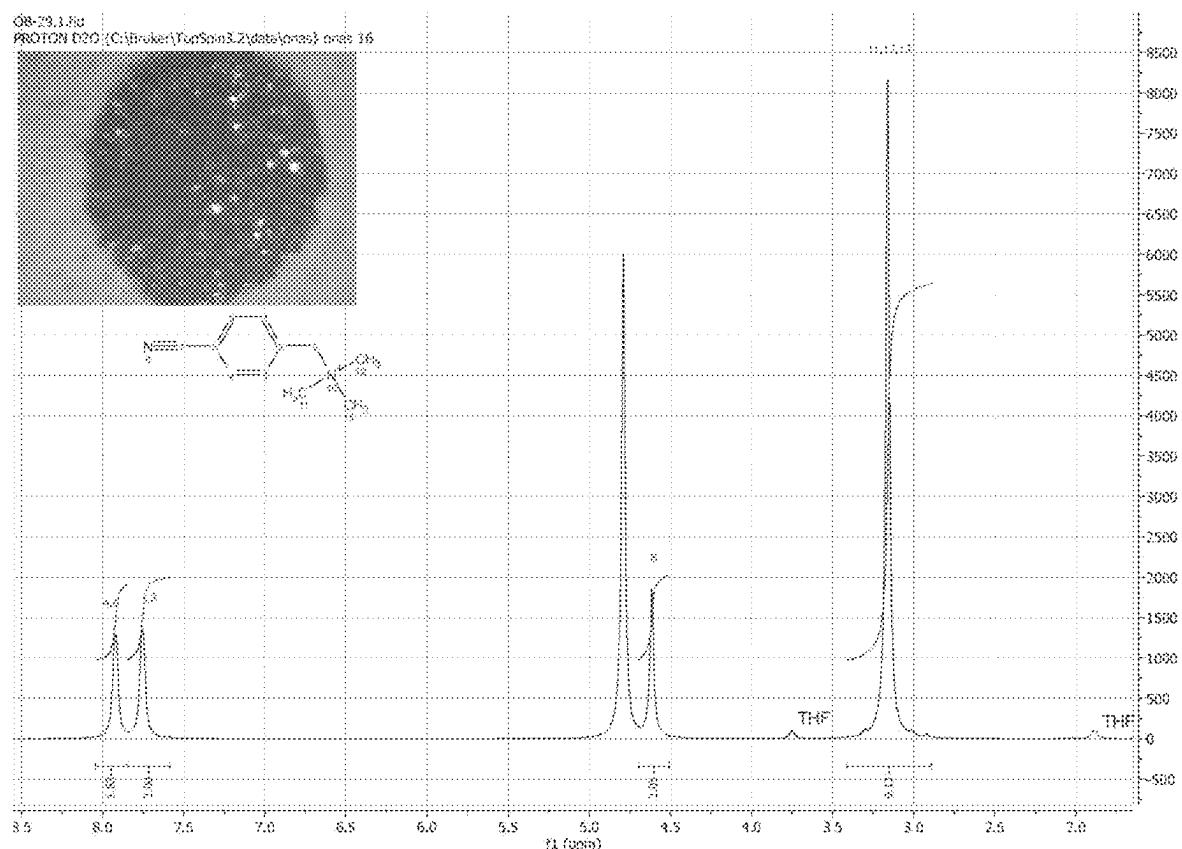


FIG. 8

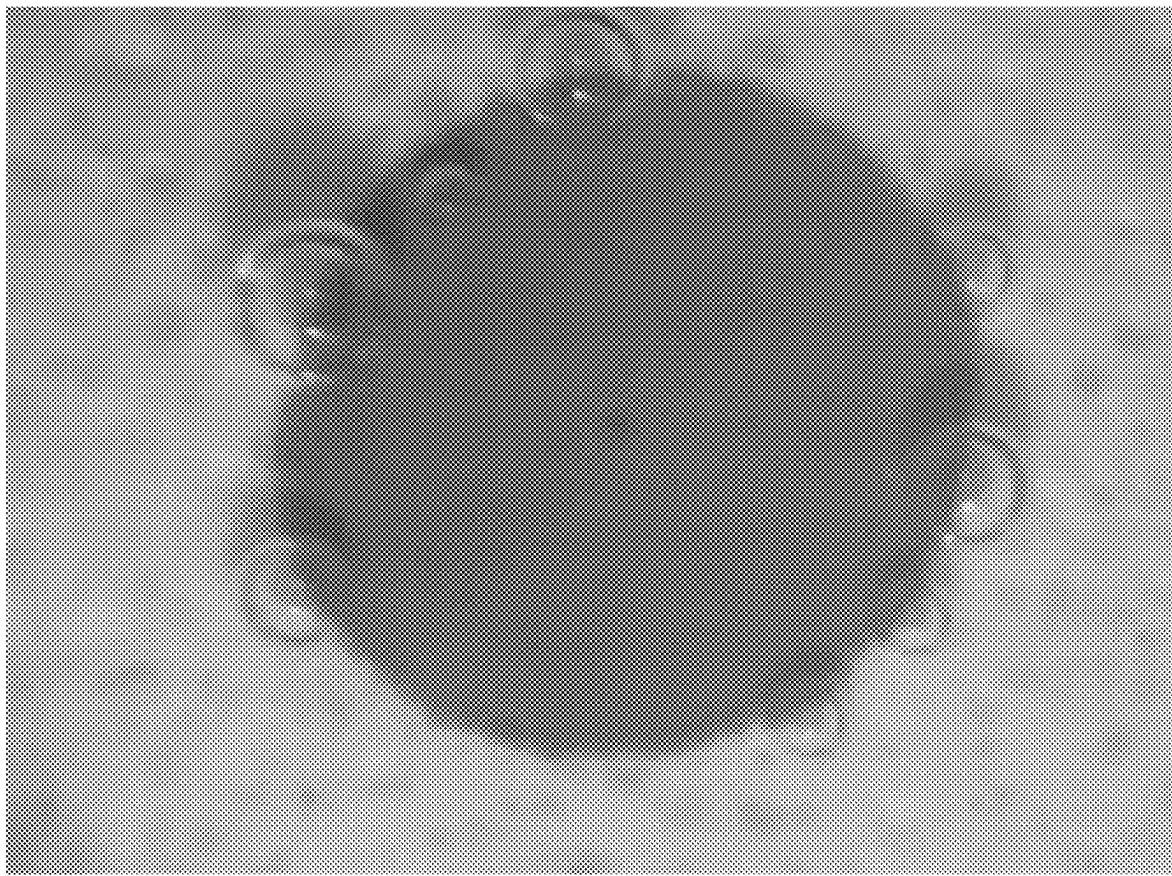


FIG. 9

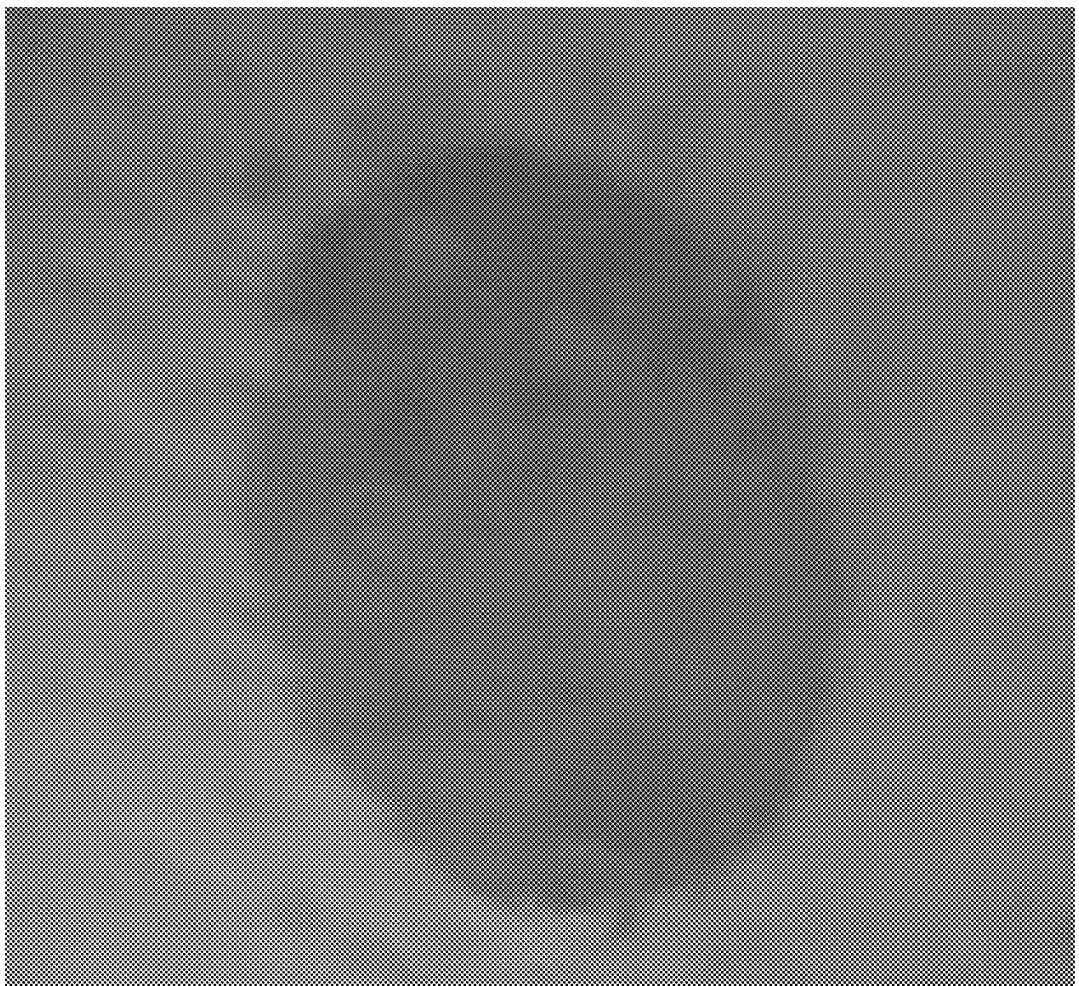


FIG. 10



FIG. 11

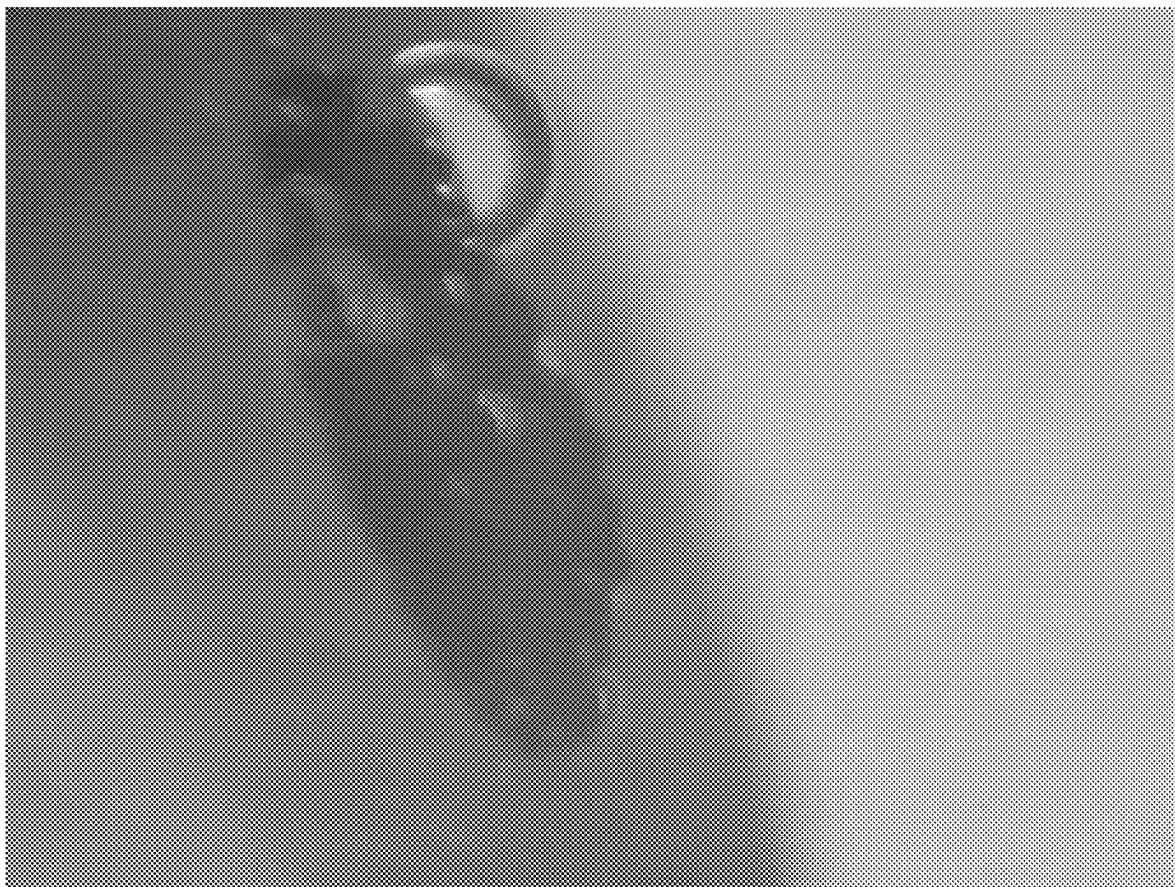


FIG. 12

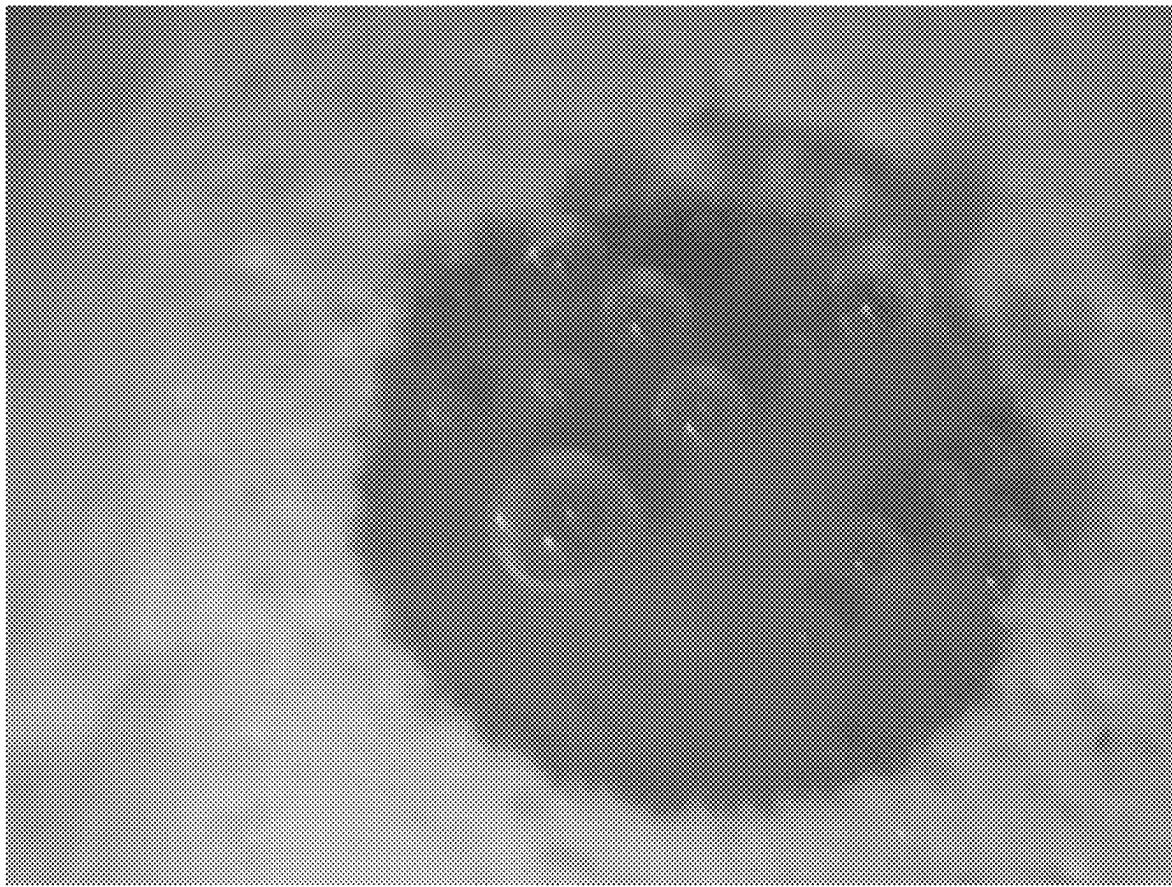


FIG. 13

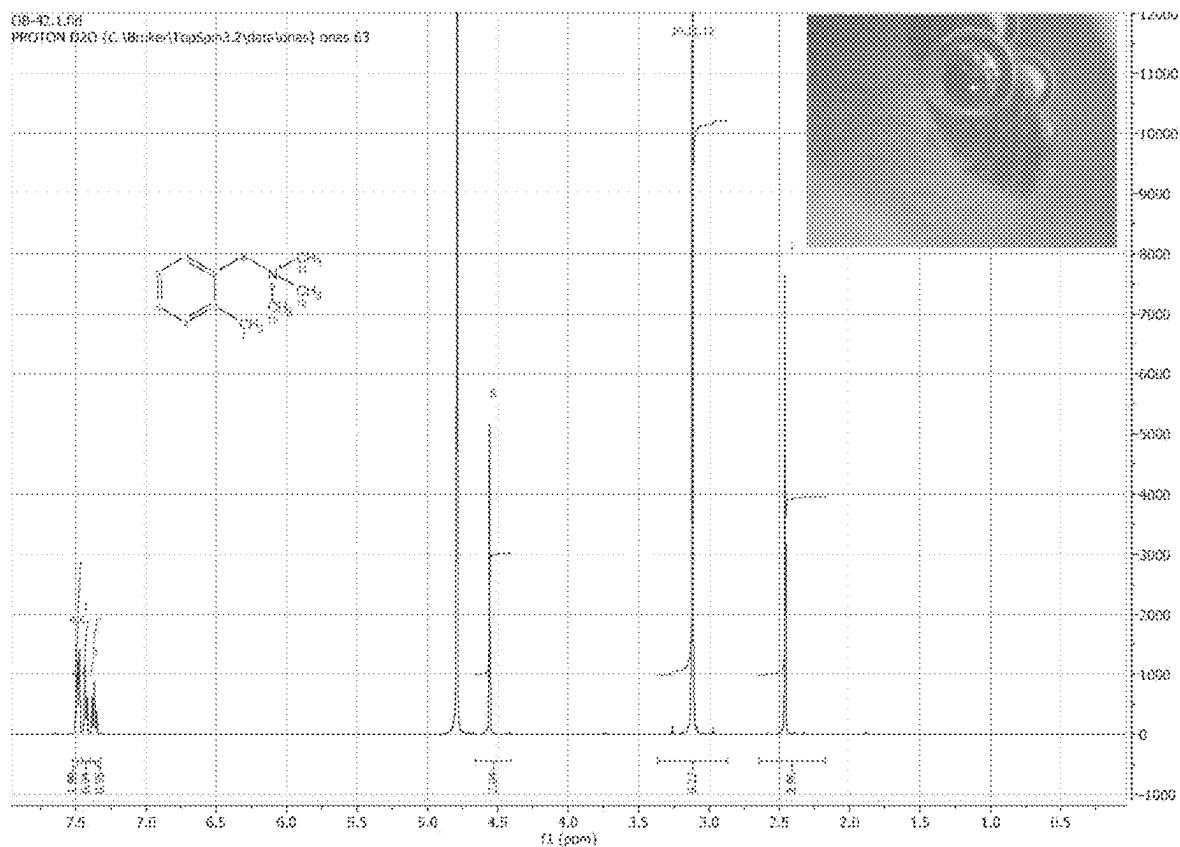


FIG. 14

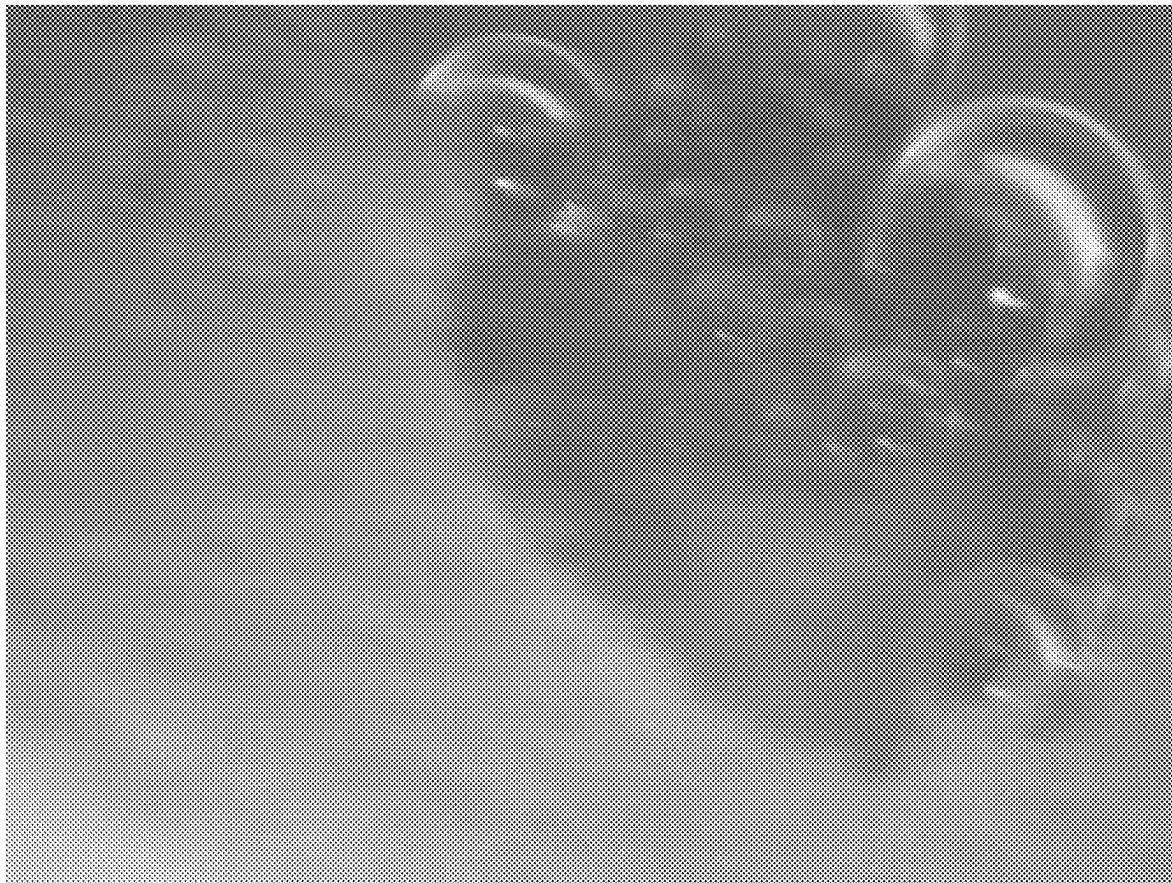


FIG. 15

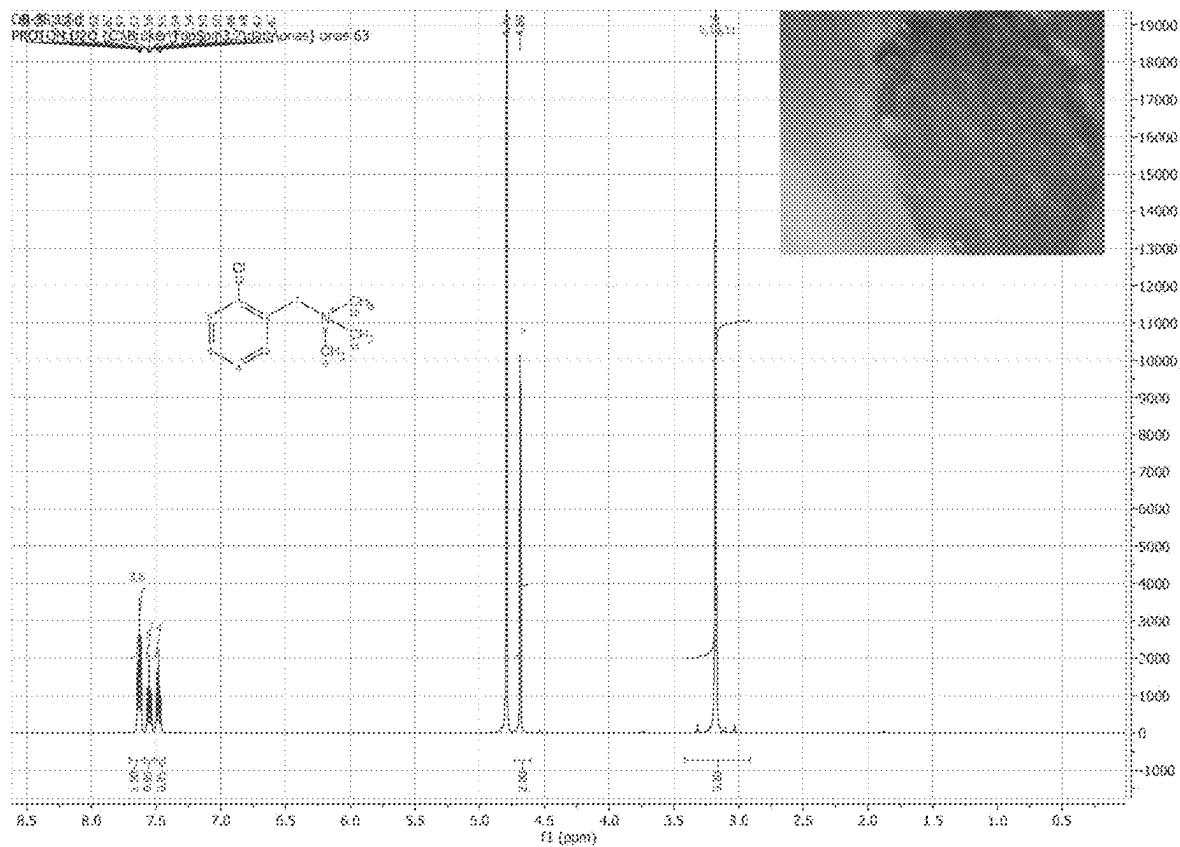


FIG. 16

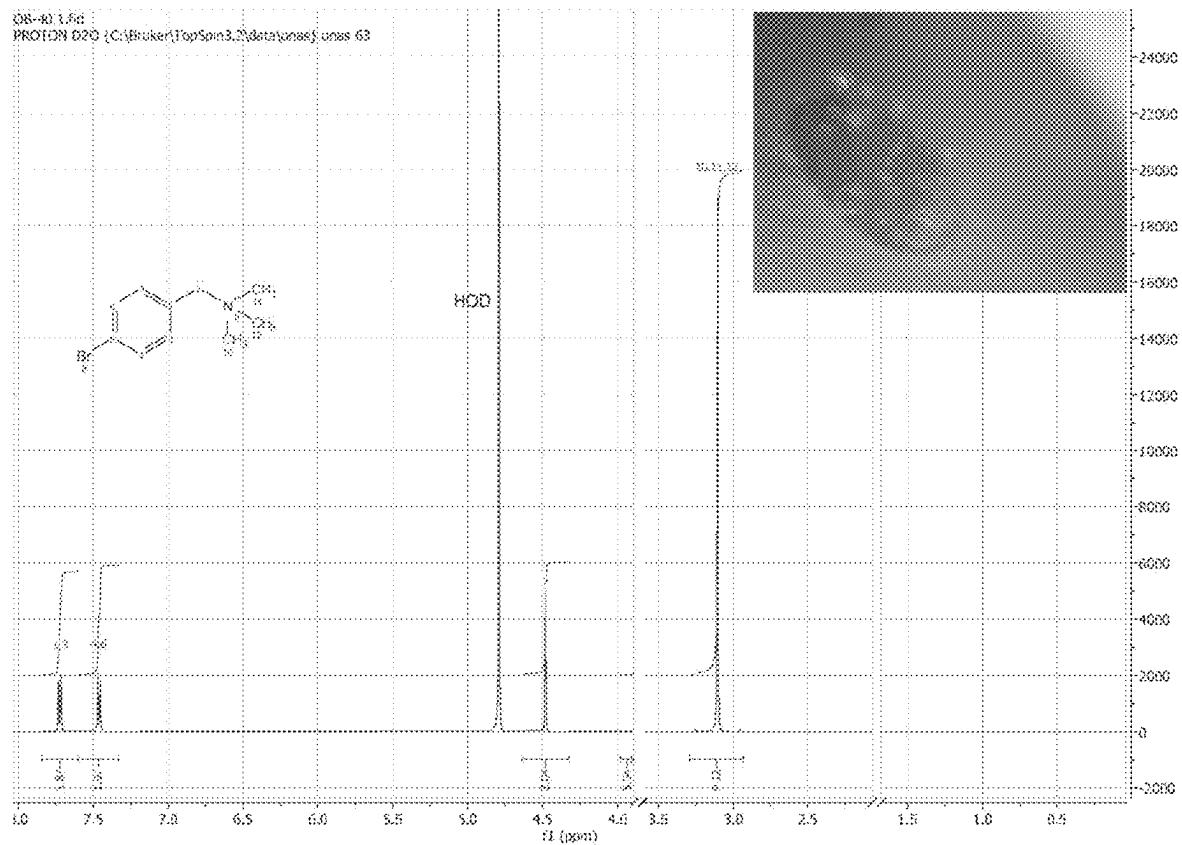


FIG. 17

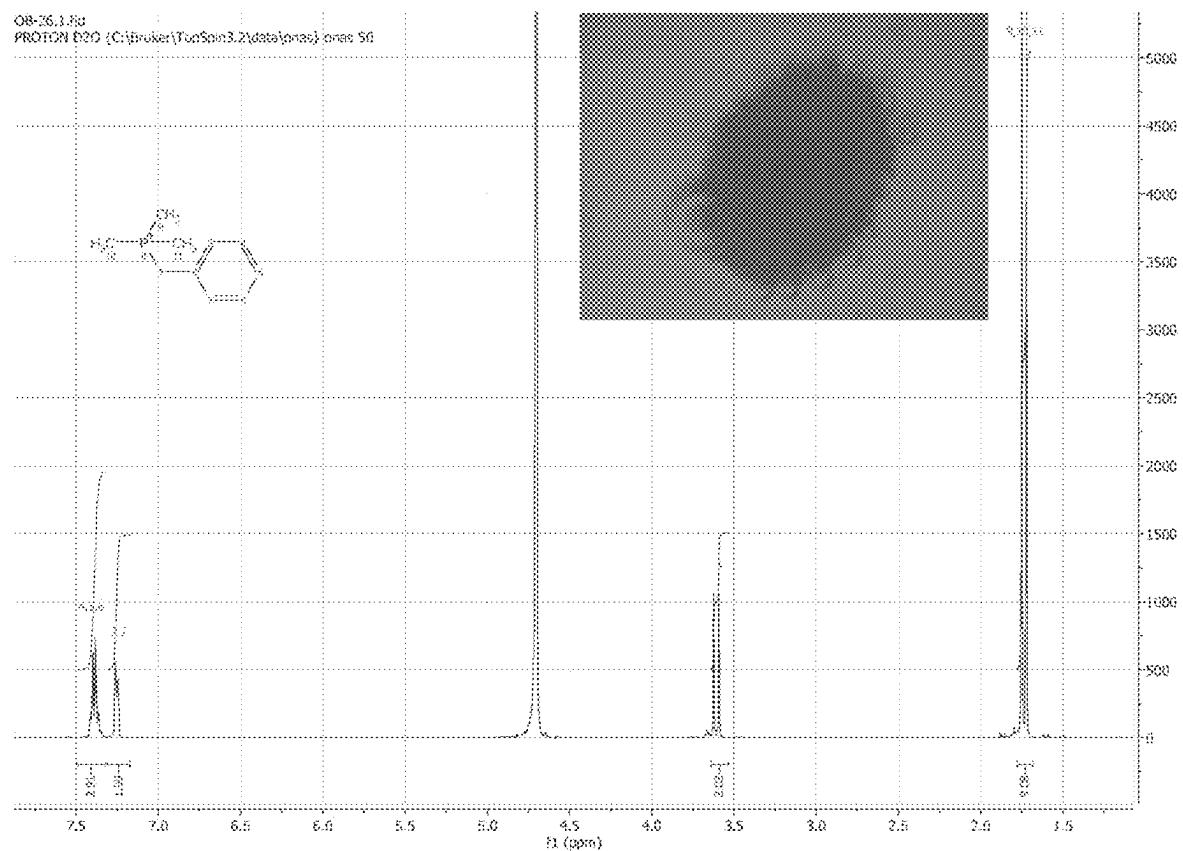


FIG. 18

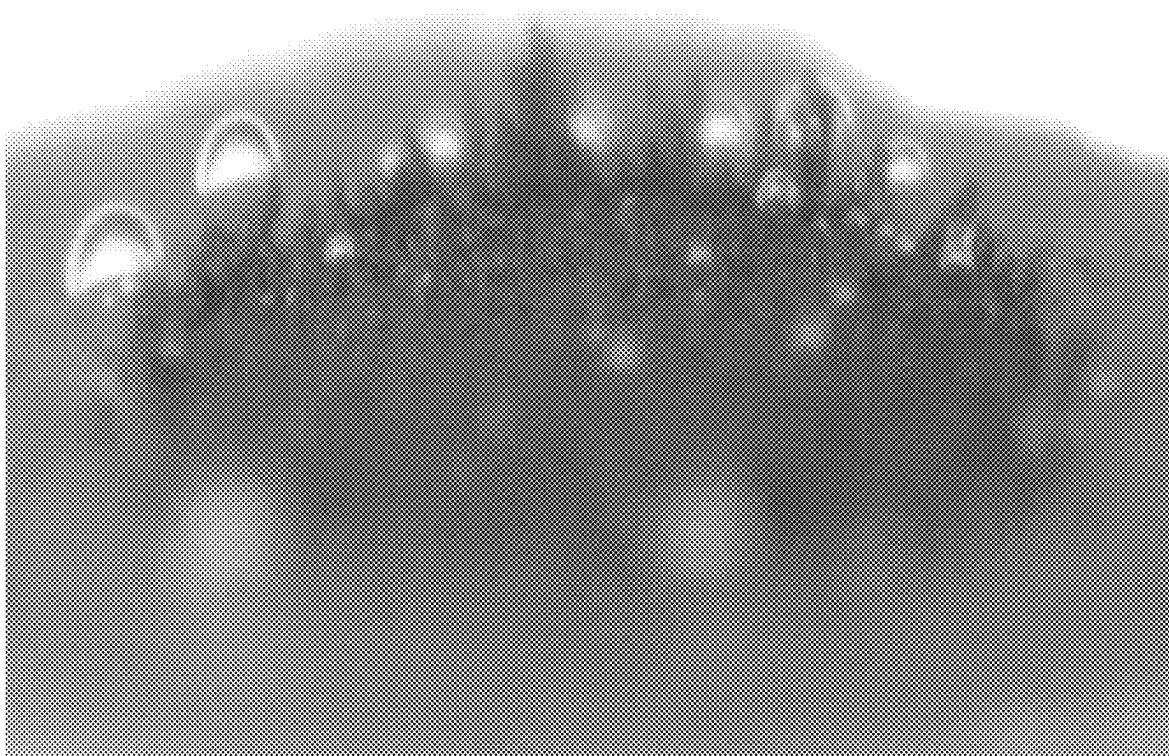


FIG. 19

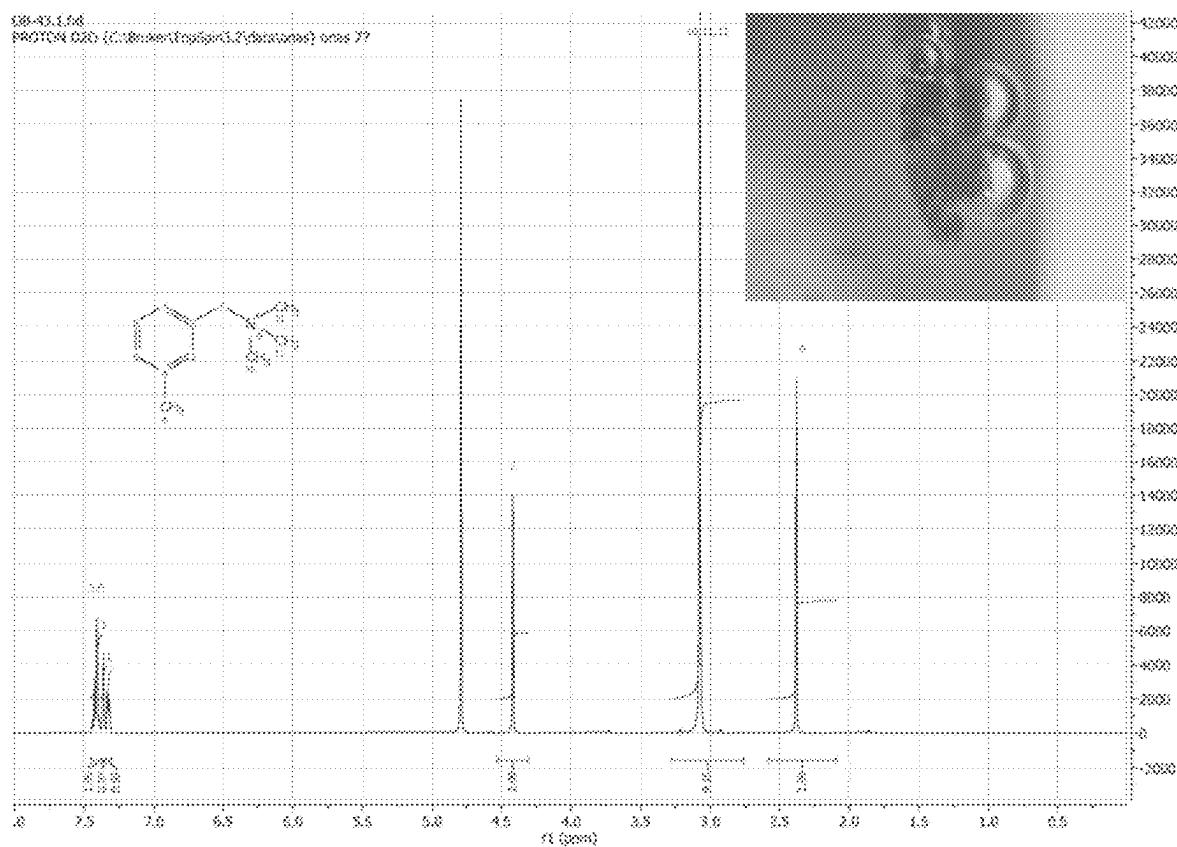


FIG. 20

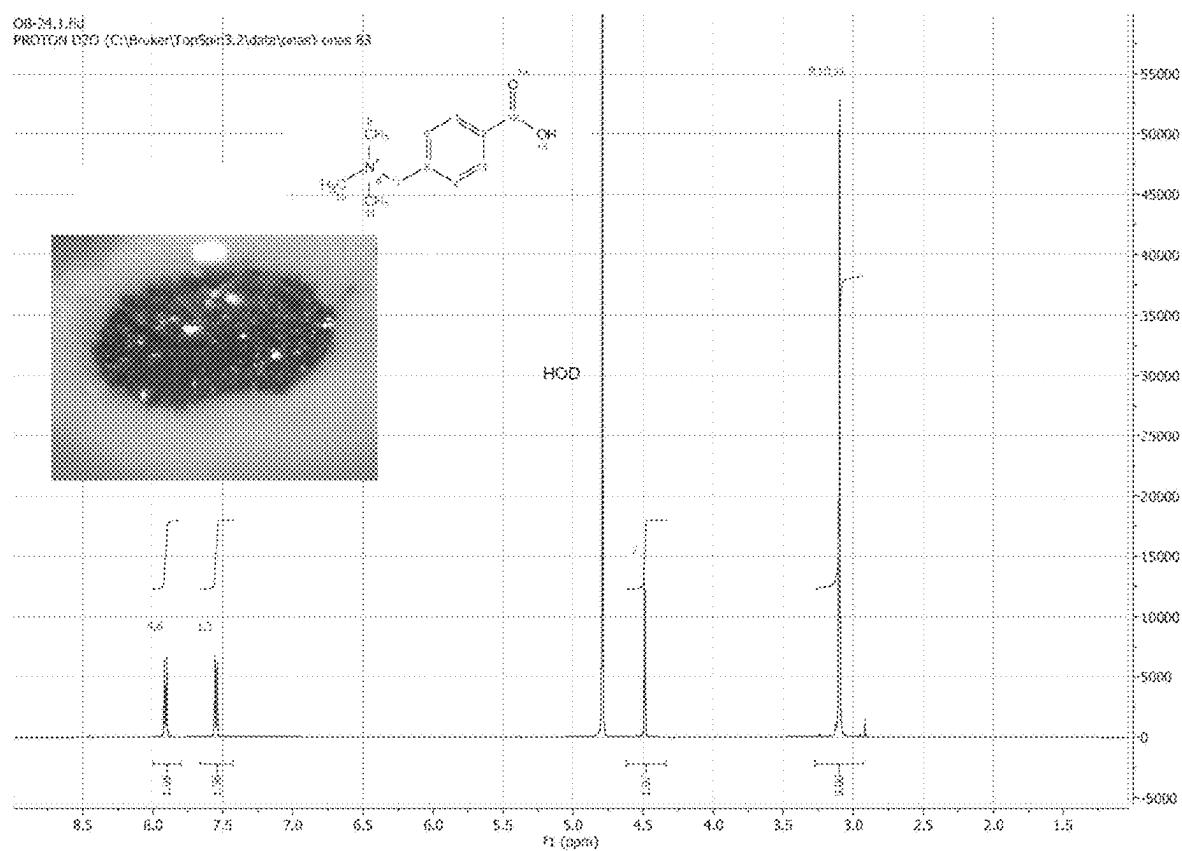


FIG. 21



FIG. 22

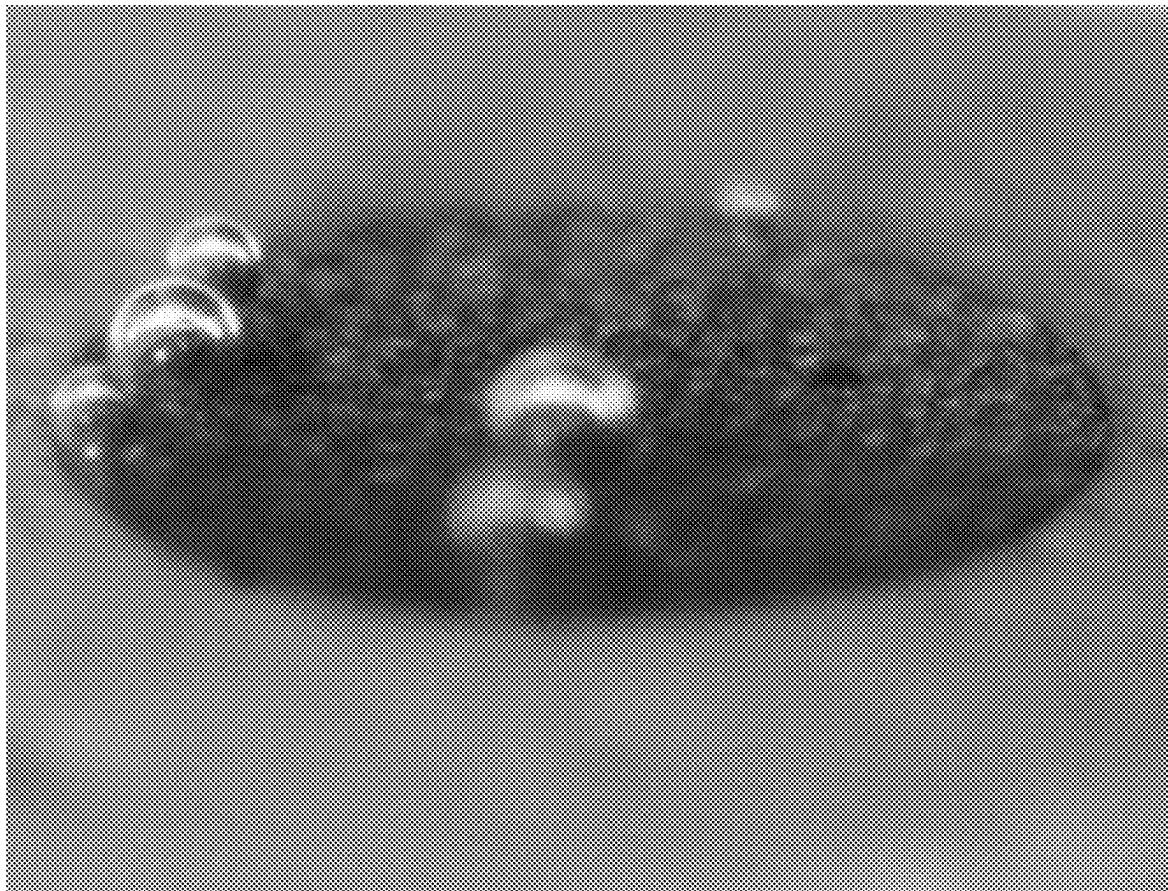


FIG. 23

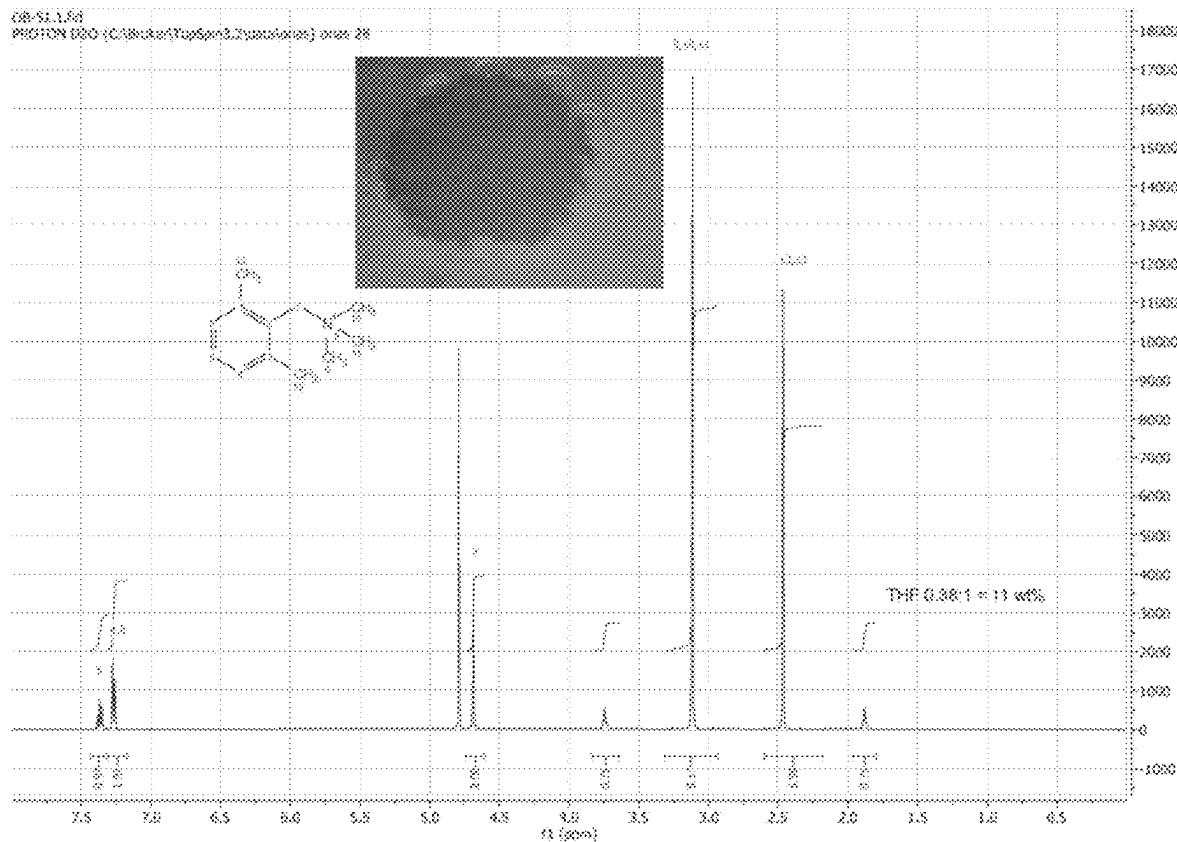


FIG. 24



FIG. 25

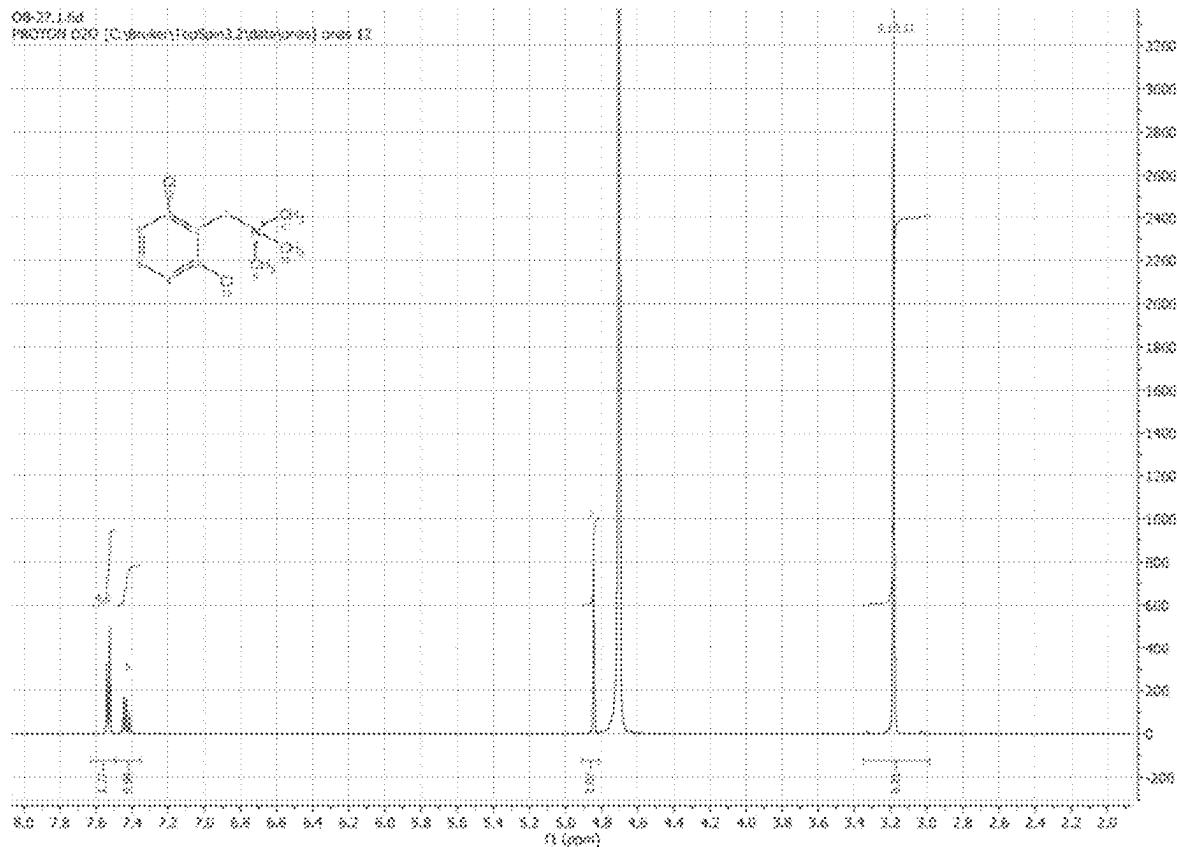


FIG. 26

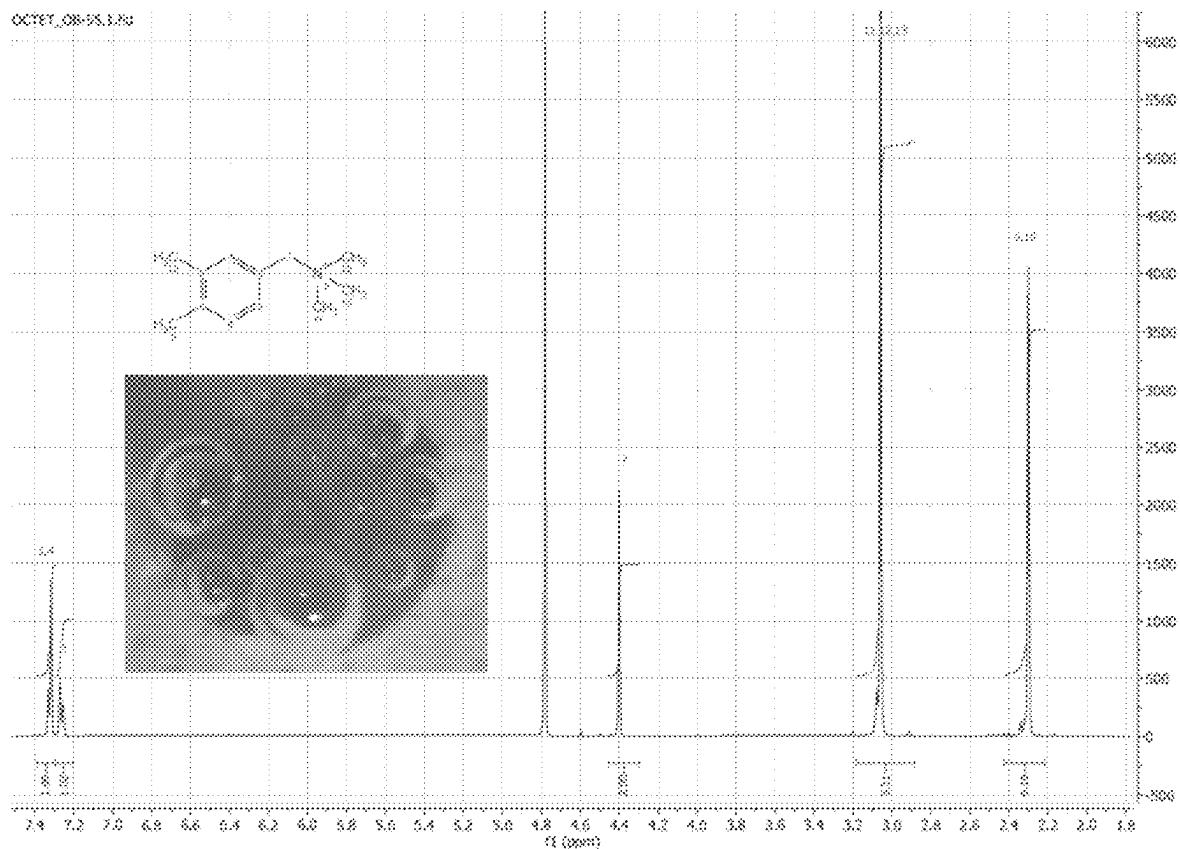


FIG. 27

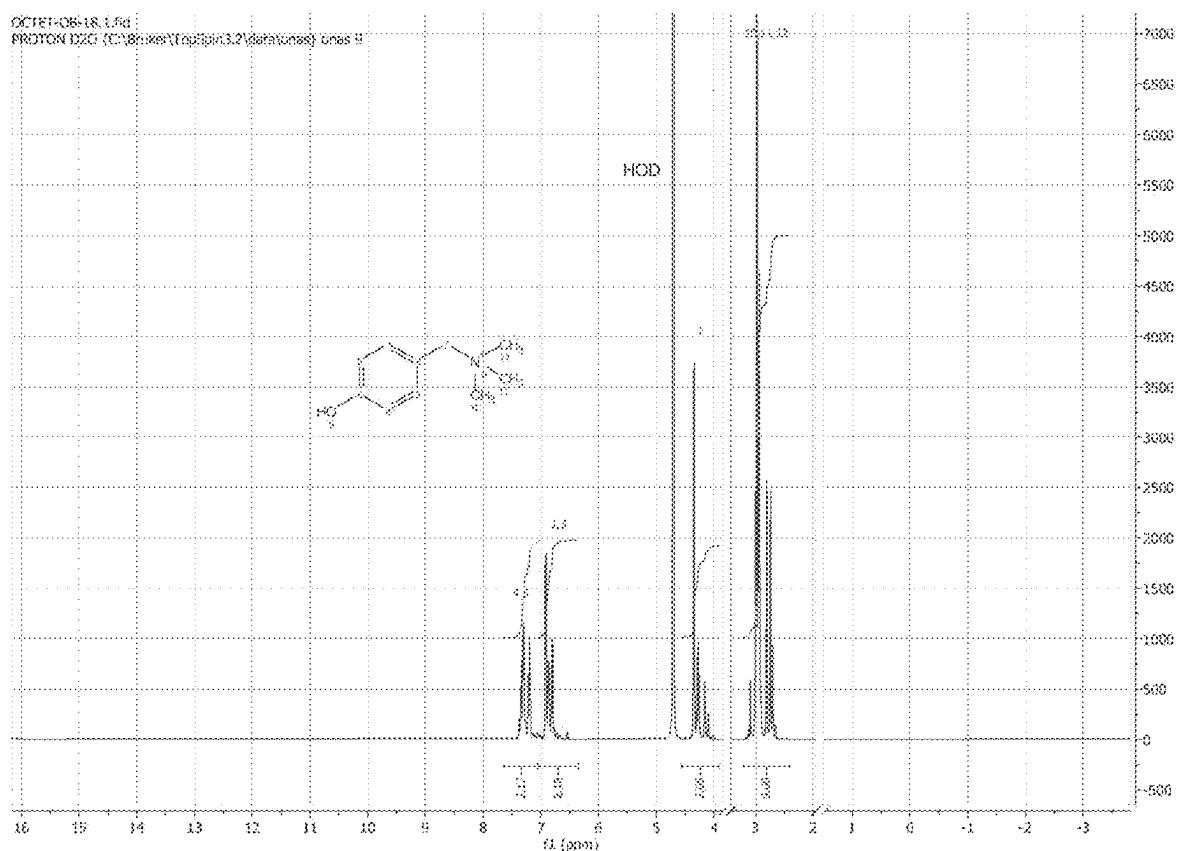


FIG. 28

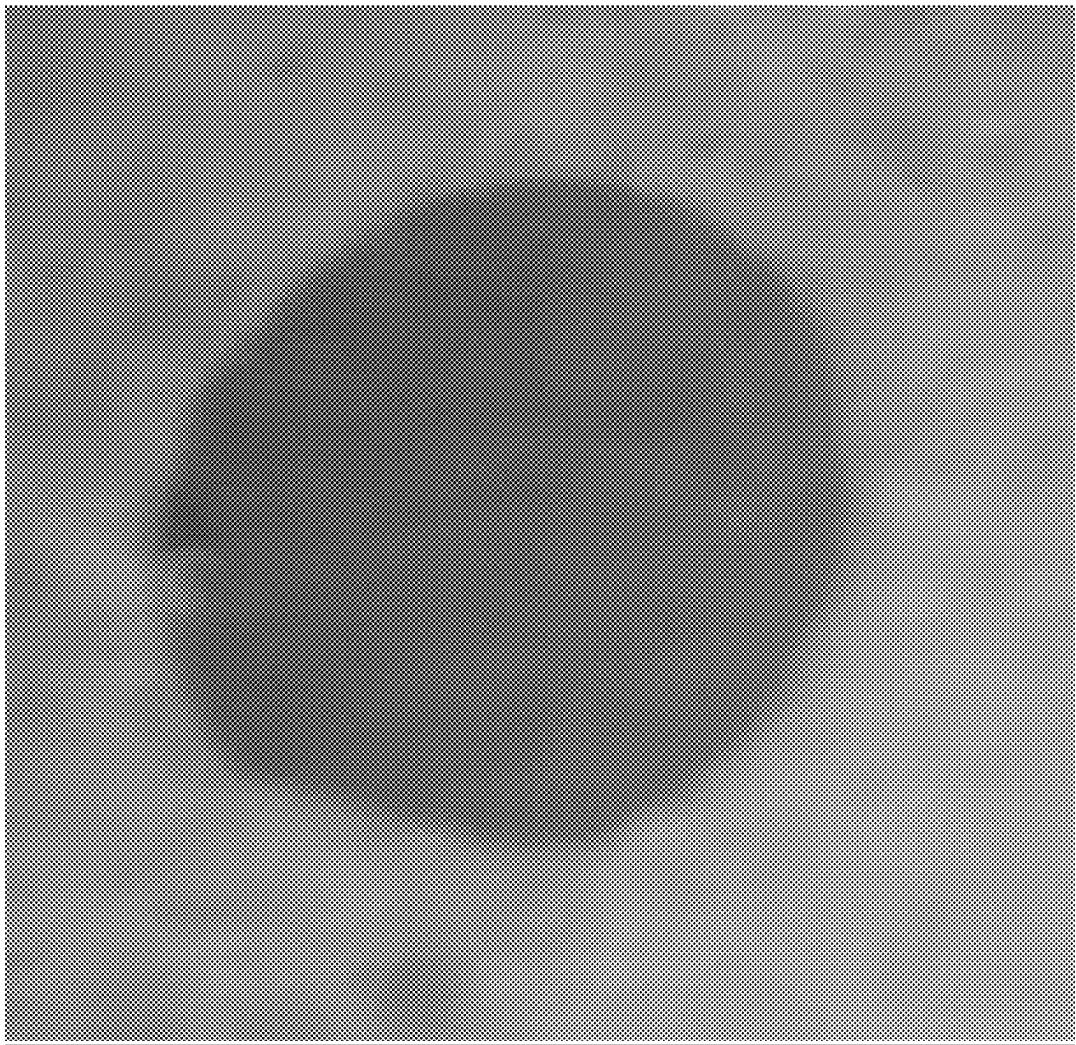


FIG. 29

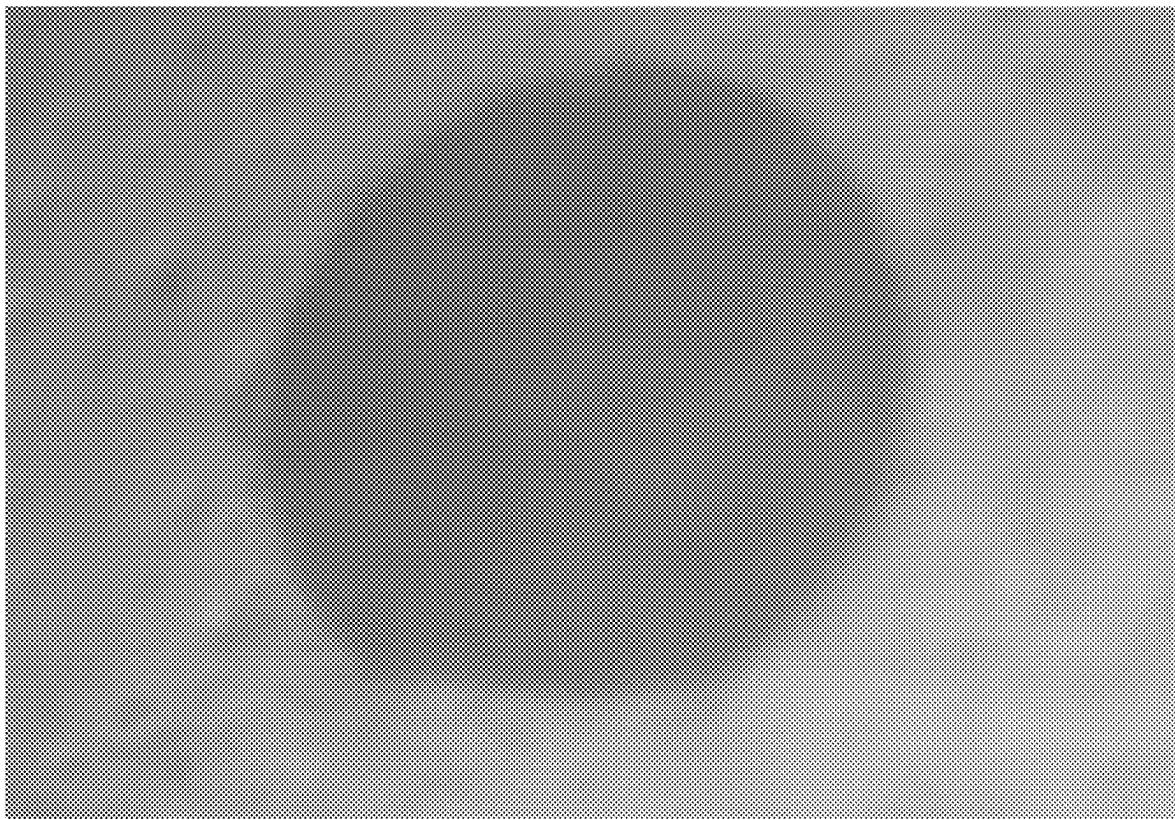


FIG. 30

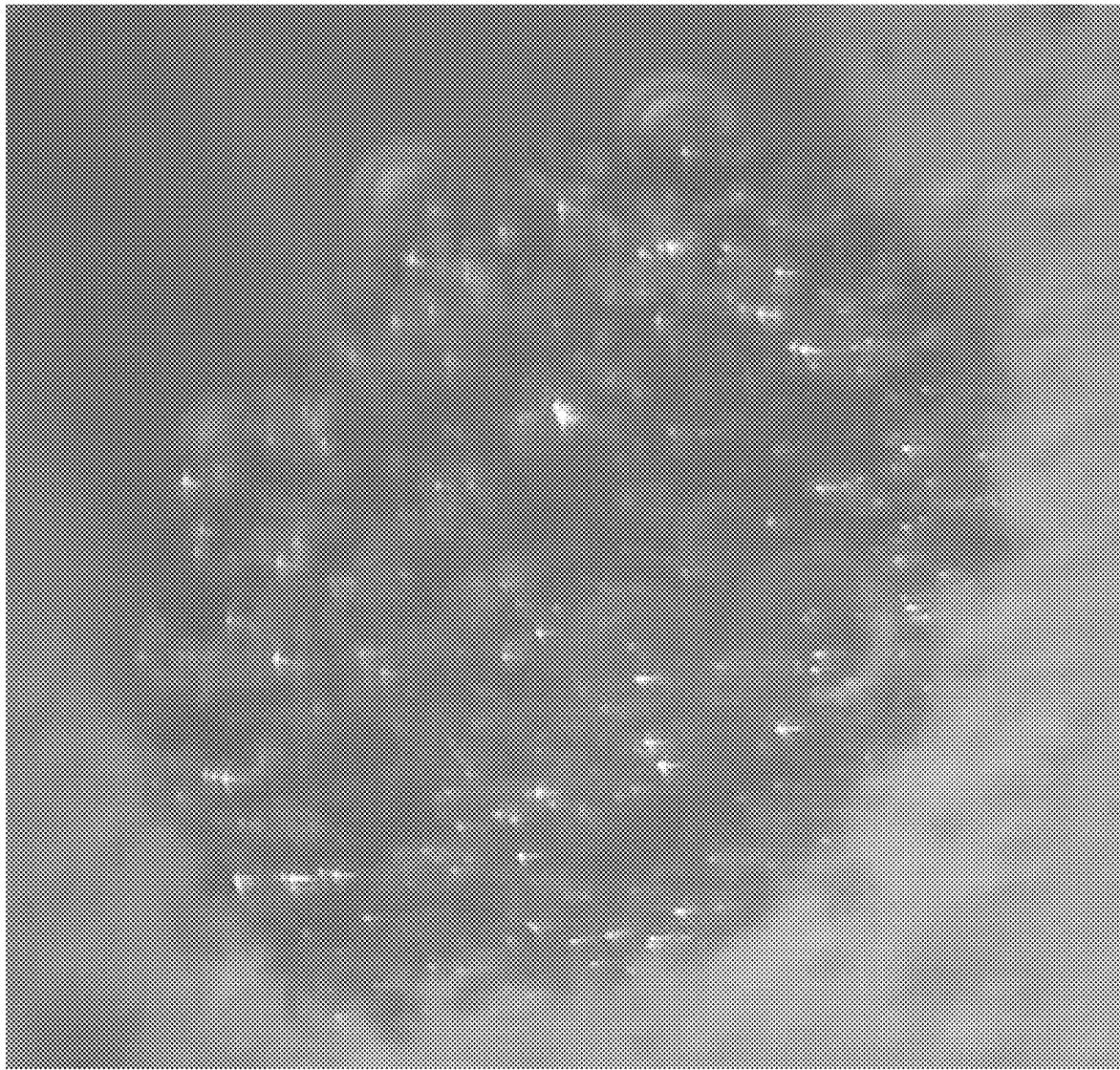


FIG. 31

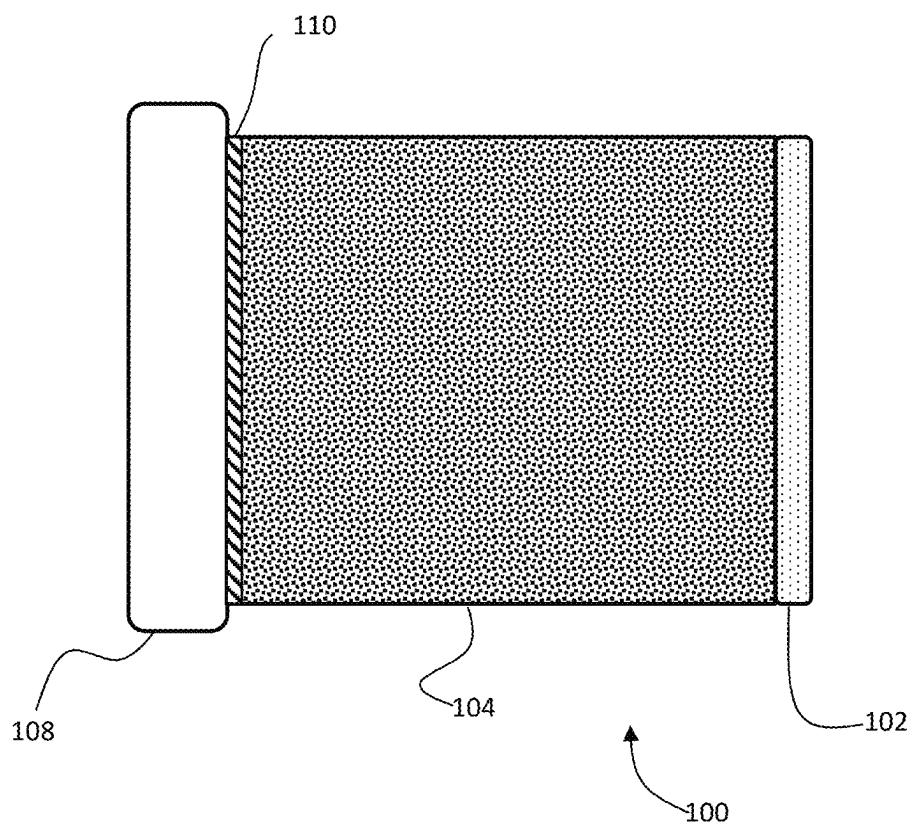


FIG. 32

ZINC BATTERY ELECTROLYTE ADDITIVE

This application is a continuation-in-part of Ser. No. 16/752,170 filed Jan. 24, 2020, which is now U.S. Pat. No. 11,424,484. Parent application Ser. No. 16/752,170 claims the benefit of U.S. Provisional Patent Application No. 62/796,296 filed on Jan. 24, 2019.

This invention was made with government support under contract number NSF 1746210 awarded by the National Science Foundation. The government has certain rights in the invention.

I. BACKGROUND OF THE INVENTION**A. Field of Invention**

The invention generally relates to chemical additives for zinc battery electrolytes.

B. Description of the Related Art

Despite their attractive cost and safety, batteries that utilize zinc as their anode material suffer from several problems intrinsic to this metal. Among these are 1) the formation of dendrites during recharging and 2) parasitic side reactions such as the evolution of hydrogen gas from the electrolyte reacting at the zinc surface. These problems have contributed to both limit the penetration of zinc batteries into certain markets and to prevent the emergence of otherwise promising zinc battery chemistries such as Zinc-Air. Dendrite formation reduces battery efficiency and can lead to cell failure. Hydrogen evolution can cause reduced shelf life due to self-discharge as well as mechanical damage due to pressure buildup.

It is known to use additives to suppress dendrite formation and hydrogen evolution; however, few known additives are effective at suppressing dendrite formation and hydrogen evolution. Moreover, known additives exhibit certain negative properties such as loss of cell efficiency. Some embodiments of the present invention may provide one or more benefits or advantages over the prior art.

II. SUMMARY OF THE INVENTION

Embodiments of the invention may relate to electrolyte additives for partially or fully suppressing dendrite formation and hydrogen evolution in zinc batteries. Embodiments include a zinc electrochemical battery cell incorporating the additives. Embodiments also include electrolyte additive chemical compositions comprising quaternary ammonium or phosphonium salts.

As used herein the terms “embodiment”, “embodiments”, “some embodiments”, “other embodiments” and so on are not exclusive of one another. Except where there is an explicit statement to the contrary, all descriptions of the features and elements of the various embodiments disclosed herein may be combined in all operable combinations thereof.

Language used herein to describe process steps may include words such as “then” which suggest an order of operations; however, one skilled in the art will appreciate that the use of such terms is often a matter of convenience and does not necessarily limit the process being described to a particular order of steps.

Conjunctions and combinations of conjunctions (e.g. “and/or”) are used herein when reciting elements and characteristics of embodiments; however, unless specifically

stated to the contrary or required by context, “and”, “or” and “and/or” are interchangeable and do not necessarily require every element of a list or only one element of a list to the exclusion of others.

5 Terms of degree, terms of approximation, and/or subjective terms may be used herein to describe certain features or elements of the invention. In each case sufficient disclosure is provided to inform the person having ordinary skill in the art in accordance with the written description requirement and the definiteness requirement of 35 U.S.C. 112.

The term “effective amount” is used herein to indicate an amount of an electrolyte additive dissolved in a liquid electrolyte that reduces dendrite formation and hydrogen evolution by a measurable and/or visually perceptible amount under the stated test conditions, or where no conditions are stated in 4M potassium hydroxide, 0.1M zinc oxide, and water at -1.6V relative to a Hg/HgO reference electrode for 1500 seconds. However, this is not intended to 15 limit the invention to the stated test conditions. The person having ordinary skill in the art would readily understand that a wide variety of electrolytes and concentrations of electrolytes, for instance, may be appropriate or desirable for a given application. It is well within the skill in the art to select 20 from known electrolytes.

III. BRIEF DESCRIPTION OF THE DRAWINGS

The invention may take physical form in certain parts and 30 arrangement of parts, embodiments of which will be described in detail in this specification and illustrated in the accompanying drawings which form a part hereof, wherein like reference numerals indicate like structure, and wherein:

FIG. 1 is a photograph of electrodeposited zinc in a 35 control cell containing no additive after operating the cell for 1500 s;

FIG. 2 is a photograph of electrodeposited zinc in a cell containing 1.0 wt % Benzyltrimethylammonium Hydroxide after operating the cell for 1500 s;

40 FIG. 3 is a photograph of electrodeposited zinc in a cell containing 1.0 wt % Benzyltributylammonium Chloride after operating the cell for 1500 s;

FIG. 4 is a photograph of electrodeposited zinc in a cell containing 1.0 wt % Dibenzylidemethylammonium Chloride after operating the cell for 1500 s;

45 FIG. 5 is a photograph of electrodeposited zinc in a cell containing 0.01 wt % Dibenzylidemethylammonium Chloride after operating the cell for 1500 s;

FIG. 6 is a photograph of electrodeposited zinc in a cell containing 0.1 wt % Dibenzylidemethylammonium Chloride after operating the cell for 1500 s;

50 FIG. 7 is ¹H NMR data for 1-(Trimethylammonium methyl)naphthalene chloride in D₂O with an inlay photograph of electrodeposited zinc in a cell containing 1.0 wt % 1-(Trimethylammonium methyl)naphthalene chloride after operating the cell for 1500 s;

FIG. 8 is ¹H NMR data for 4-(Trimethylammonium methyl)benzonitrile Chloride in D₂O with an inlay photograph of electrodeposited zinc in a cell containing 1.0 wt % 4-(Trimethylammonium methyl)benzonitrile Chloride after operating the cell for 1500 s;

55 FIG. 9 is a photograph of electrodeposited zinc in a cell containing 1.0 wt % 4-(Trimethylammonium methyl)anisole Chloride after operating the cell for 1500 s;

FIG. 10 is a photograph of electrodeposited zinc in a cell containing 0.5 wt % 4-(Trimethylammonium methyl)anisole Chloride after operating the cell for 1500 s;

FIG. 11 is a photograph of electrodeposited zinc in a cell containing 0.1 wt % 4-(Trimethylammonium methyl)anisole Chloride after operating the cell for 1500 s;

FIG. 12 is a photograph of electrodeposited zinc in a cell containing 1.0 wt % 4-(Trimethylammonium methyl)-1,2,6-trimethoxybenzene after operating the cell for 1500 s;

FIG. 13 is a photograph of electrodeposited zinc in a cell containing 1.0 wt % (4-Methylbenzyl)trimethylammonium Chloride after operating the cell for 1500 s;

FIG. 14 is ^1H NMR data for (2-Methylbenzyl)trimethylammonium Chloride in D_2O with an inlay photograph of electrodeposited zinc in a cell containing 1.0 wt % (2-Methylbenzyl)trimethylammonium Chloride after operating the cell for 1500 s;

FIG. 15 is a photograph of electrodeposited zinc in a cell containing 1.0 wt % (4-Chlorobenzyl)trimethylammonium Chloride after operating the cell for 1500 s;

FIG. 16 is ^1H NMR data for (2-Chlorobenzyl)trimethylammonium Chloride in D_2O with an inlay photograph of electrodeposited zinc in a cell containing 1.0 wt % (2-Chlorobenzyl)trimethylammonium Chloride after operating the cell for 1500 s;

FIG. 17 is ^1H NMR data for (4-Bromobenzyl)trimethylammonium Bromide in D_2O with an inlay photograph of electrodeposited zinc in a cell containing 1.0 wt % (4-Bromobenzyl)trimethylammonium Bromide after operating the cell for 1500 s;

FIG. 18 is ^1H NMR data for Benzyltrimethylphosphonium Chloride in D_2O with an inlay photograph of electrodeposited zinc in a cell containing 1.0 wt % Benzyltrimethylphosphonium Chloride after operating the cell for 1500 s;

FIG. 19 is a photograph of electrodeposited zinc in a cell containing 1.0 wt % (2-Hydroxybenzyl)trimethylammonium Iodide after operating the cell for 1500 s;

FIG. 20 is ^1H NMR data for (3-Methylbenzyl)trimethylammonium Chloride in D_2O with an inlay photograph of electrodeposited zinc in a cell containing 1.0 wt % (3-Methylbenzyl)trimethylammonium Chloride after operating the cell for 1500 s;

FIG. 21 is ^1H NMR data for 4-(Trimethylammonium)benzoic acid Bromide in D_2O with an inlay photograph of electrodeposited zinc in a cell containing 1.0 wt % 4-(Trimethylammonium methyl)benzoic acid Bromide after operating the cell for 1500 s;

FIG. 22 is a photograph of electrodeposited zinc in a cell containing 1.0 wt % 3-(Trimethylammonium methyl)anisole Chloride after operating the cell for 1500 s;

FIG. 23 is a photograph of electrodeposited zinc in a cell containing 1.0 wt % Benzalkonium Chloride after operating the cell for 1500 s;

FIG. 24 is ^1H NMR data for (2,6-Dimethylbenzyl)trimethylammonium Chloride in D_2O with an inlay photograph of electrodeposited zinc in a cell containing 1.0 wt % (2,6-Dimethylbenzyl)trimethylammonium;

FIG. 25 is a photograph of electrodeposited zinc in a cell containing 25 wt % Benzyltrimethylammonium chloride after operating the cell for 1500 s;

FIG. 26 is ^1H NMR data for (2,6-Dichlorobenzyl)trimethylammonium chloride in D_2O ;

FIG. 27 is ^1H NMR data for (3,4-Dimethylbenzyl)trimethylammonium chloride in D_2O with an inlay photograph of electrodeposited zinc in a cell containing 1.0 wt % (3,4-Dimethylbenzyl)trimethylammonium chloride after operating the cell for 1500 s;

FIG. 28 is ^1H NMR data for (4-Hydroxybenzyl)trimethylammonium Iodide in D_2O ;

FIG. 29 is a photograph of electrodeposited zinc in a cell containing 15 wt % 4-(Trimethylammoniummethyl)anisole chloride after operating the cell for 1500 s;

FIG. 30 is a photograph of electrodeposited zinc in a cell containing 15 wt % (4-Methylbenzyl)trimethylammonium chloride after operating the cell for 1500 s;

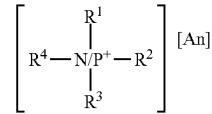
FIG. 31 is a photograph of electrodeposited zinc in a cell containing 0.1 wt % (4-Methylbenzyl)trimethylammonium chloride after operating the cell for 1500 s; and

FIG. 32 is a schematic view of a general zinc-based battery in accordance with one or more embodiments of the invention.

IV. DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the invention include organic electrolyte additives that improve zinc battery performance by both selectively preventing dendrite formation and preventing hydrogen evolution side reactions without hindering cell efficiency. Embodiments may include quaternary nitrogen and/or phosphorous compounds substituted with a variety of linear and/or cyclic organic groups.

Formula I illustrates an embodiment of the invention comprising a central nitrogen or phosphorous atom with a charge of +1, denoted herein as “N/P⁺” or as an “N/P⁺ center”. The N/P⁺ center is bonded to four R groups R¹, R², R³, and R⁴. The structure shown in Formula I is not intended to illustrate isomers or stereochemical structures, but rather is intended to encompass all isomeric forms with the same atom-to-atom connectivity.



Irup xod#L

R¹ is selected from the following radicals, where “yl” or “methylene” refers to the position of the radical electron available for bonding with an N/P⁺ center: methyl benzene, 4-methylene-toluene, 3-methylene-toluene, 2-methylene-toluene, 4-methylene-chlorobenzene, 3-methylene-chlorobenzene, 2-methylene-chlorobenzene, 4-methylene-bromobenzene, 3-methylene-bromobenzene, 2-methylene-bromobenzene, 4-methylene-iodobenzene, 3-methylene-iodobenzene, 2-methylene-iodobenzene, 4-methylene-cyanobenzene, 3-methylene-cyanobenzene, 2-methylene-cyanobenzene, 4-methylene-anisole, 3-methylene-anisole, 2-methylene-anisole, 1-methylnaphthalene, 1-methylene-2,6-dimethylbenzene, 1-methylene-2,4-dimethylbenzene, 1-methylene-3,4-dimethylbenzene, 1-methylene-2,5-dimethylbenzene, 1-methylene-3,5-dimethylbenzene, 1-methylene-2,4,6-trimethylbenzene, 1-methylene-3,4,5-trimethoxybenzene, 1-methylene-2,6-dichlorobenzene, 4-methylene-nitrobenzene, 4-methylene-benzoic acid, 3-methylene-benzoic acid, 2-methylene-benzoic acid, 2-methylene-phenol, 3-methylene-phenol, and 4-methylene-phenol.

With continuing reference to Formula I, the radicals R², R³, and R⁴ may be independently selected from R¹, methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-octyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, or n-octadecyl. Radicals R², R³, and R⁴ may be independently selected from linear and non-linear alkyls from C1 to C25.

Embodiments conforming to Formula I may include a sufficient amount of counter anion [An] to produce a neutral species. The anion [An] may be, for example and without limitation, chloride, bromide, iodide, fluoride, hydroxide, nitrate, nitrite, sulphate, sulphite, phosphate, perchlorate, or any combination thereof. The person having ordinary skill in the art will readily appreciate that the anion has less or no influence on performance of the electrolyte additives of the present invention. Accordingly, a wide variety of anions are within the scope of the invention, and the foregoing list is meant only to be illustrative.

Referring now to the drawings wherein the showings are for purposes of illustrating embodiments of the invention only and not for purposes of limiting the same, FIG. 1 is a photograph showing dendrite growth using 4M KOH, 0.1M ZnO, and water with no additives suppressing dendrite growth. Plating was conducted at -1.6V relative to a Hg/HgO reference electrode for 1500 seconds. FIG. 1 shows dendrite growth after 1500 seconds. This serves as a control

against which dendrite suppression additives are compared in subsequent tests. Each experimental run is conducted under the same conditions as the control run, namely, in 4M KOH electrolyte, 0.1M ZnO, and water at -1.6V relative to a Hg/HgO reference electrode for 1500 seconds. The results are summarized in Table I.

With respect to the control results shown in FIG. 1, prominent dendrite growth is clearly visible. Although the control rapidly evolves hydrogen, the bubbles form so quickly over the entire surface that they do not adhere to the dendrites. Accordingly, very few if any hydrogen bubbles are visible in FIG. 1. In contrast FIGS. 2-18 all show suppression of hydrogen evolution to some degree, which may be complete hydrogen suppression or partial hydrogen suppression. Where hydrogen suppression is complete, no bubbles form on the plated zinc surface so the associated figure shows no hydrogen bubbles. However, where hydrogen evolution is partially suppressed large slow-forming hydrogen bubbles are visible in the associated figure adhering to the plated zinc.

TABLE I

Suppression of Dendrite Formation by Additives				
Additive	Amount (wt %)	Hydrogen Suppressed	Dendrite Suppressed	FIG.
No additive (control)	0	No	No	FIG. 1
Benzyltrimethylammonium Hydroxide (BTMAH)	1.0	Partial	Yes	FIG. 2
Benzyltributylammonium Chloride (BTBAC)	1.0	Partial	Yes	FIG. 3
Dibenzylidimethylammonium Chloride (DBDMAC)	1.0	Partial	Yes	FIG. 4
Dibenzylidimethylammonium Chloride (DBDMAC)	0.01	No	Partial	FIG. 5
Dibenzylidimethylammonium Chloride (DBDMAC)	0.1	Partial	Yes	FIG. 6

TABLE I-continued

Suppression of Dendrite Formation by Additives				
Additive	Amount (wt %)	Hydrogen Suppressed	Dendrite Suppressed	FIG.
1-(Trimethylammonium methyl)naphthalene Chloride (TMAMNC)	1.0	No	Partial	FIG. 7
4-(Trimethylammoniummethyl)benzonitrile Chloride (TMAMBC)	1.0	Yes	Partial	FIG. 8
4-(Trimethylammoniummethyl)anisole Chloride	1.0	Yes	Yes	FIG. 9
4-(Trimethylammoniummethyl)anisole Chloride	0.5	Partial	Yes	FIG. 10
4-(Trimethylammoniummethyl)anisole Chloride	0.1	Partial	Partial	FIG. 11
4-(Trimethylammoniummethyl)-1,2,6-trimethoxybenzene	1.0	Partial	Yes	FIG. 12

TABLE I-continued

Suppression of Dendrite Formation by Additives				
Additive	Amount (wt %)	Hydrogen Suppressed	Dendrite Suppressed	FIG.
(4-Methylbenzyl)trimethylammonium Chloride	1.0	Partial	Yes	FIG. 13
(4-Methylbenzyl)trimethylammonium chloride	15	Yes	Yes	FIG. 30
(4-Methylbenzyl)trimethylammonium chloride	0.1	Partial	Partial	FIG. 31
(2-Methylbenzyl)trimethylammonium Chloride	1.0	Partial	Yes	FIG. 14
(4-Chlorobenzyl)trimethylammonium Chloride	1.0	Partial	Partial	FIG. 15
(2-Chlorobenzyl)trimethylammonium Chloride	1.0	No	Partial	FIG. 16

TABLE I-continued

Suppression of Dendrite Formation by Additives

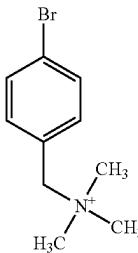
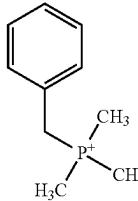
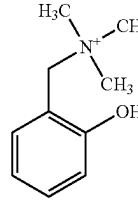
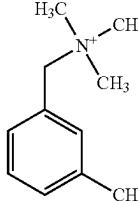
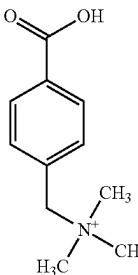
Additive	Amount (wt %)	Hydrogen Suppressed	Dendrite Suppressed	FIG.
(4-Bromobenzyl)trimethylammonium Bromide	1.0	Partial	Yes	FIG. 17
				
Benzyltrimethylphosphonium Chloride	1.0	No	Partial	FIG. 18
				
(2-Hydroxybenzyl)trimethylammonium Iodide	1.0	Partial	Partial	FIG. 19
				
(3-Methylbenzyl)trimethylammonium Chloride	1.0	Partial	Yes	FIG. 20
				
4-(Trimethylammoniummethyl)benzoic acid Bromide	1.0	Partial	Partial	FIG. 21
				

TABLE I-continued

Suppression of Dendrite Formation by Additives				
Additive	Amount (wt %)	Hydrogen Suppressed	Dendrite Suppressed	FIG.
3-(Trimethylammoniummethyl)anisole Chloride	1.0	Partial	Partial	FIG. 22
Benzalkonium Chloride	1.0	Partial	Yes	FIG. 23
(2,6-Dimethylbenzyl)trimethylammonium Chloride	1.0	No	Partial	FIG. 24
Benzyltrimethylammonium Hydroxide (BTMAH)	25	Yes	Yes	FIG. 25
(2,6-Dichlorobenzyl)trimethylammonium Chloride	1.0	Partial	No	FIG. 26
(3,4-Dimethylbenzyl)trimethylammonium Chloride	1.0	Yes	Yes	FIG. 27

TABLE I-continued

Suppression of Dendrite Formation by Additives				
Additive	Amount (wt %)	Hydrogen Suppressed	Dendrite Suppressed	FIG.
(4-Hydroxybenzyl)trimethylammonium Iodide	1.0	Partial	Partial	FIG. 28
4-(Trimethylammoniummethyl)anisole Chloride	15	Yes	Yes	FIG. 29

Dibenzylidimethylammonium chloride (DBDMAC) preparation and performance.

N,N-dimethylbenzylamine (2 g, 14.8 mmol) is diluted into 10 mL of acetonitrile and stirred under air. Benzylchloride (2.06 g, 1.87 mL, 16.3 mmol) is added at once and the reaction is heated to 78° C. to reflux for 3 hours. The solution is concentrated under reduced pressure to a colorless viscous oil. The desired product is recrystallized from acetone. A white/colorless crystal solid of 3.50 g is collected (90.4% yield) and its structure is confirmed by ¹H NMR. The dendrite suppressive effect of this additive is shown in FIGS. 4-6. Full dendrite suppression occurs at 1 wt % and 0.1 wt %, and partial suppression is observed at 0.01 wt %. Hydrogen evolution is partially suppressed at 1 wt % and 0.1 wt %. No hydrogen suppression is observed at 0.01 wt %.

1-(Trimethylammonium Methyl)Naphthalene Chloride Preparation and Performance.

To a 100 mL flask is added 10 mL of a 13% solution of trimethylamine in tetrahydrofuran (1.16 g, 19.7 mmol). The solution is stirred under air at room temperature. 1-(Chloromethyl)naphthalene (3.80 g, 3.22 mL, 21.5 mmol) is added in four quick portions and the reaction is heated to 60° C. for 3 hours. The reaction is then cooled to room temperature and white precipitates are collected by suction filtration and washed with additional tetrahydrofuran. About 3.10 g of white fluffy powder is collected (67% yield), and the desired product structure is confirmed by ¹H NMR. The partial dendrite suppressive effect of this additive is shown in FIG. 7. 1-(Trimethylammonium methyl)naphthalene chloride promotes, rather than suppresses, hydrogen evolution.

35 4-(Trimethylammoniummethyl)Benzonitrile Chloride Preparation and Performance.

To a 100 mL flask is added 10 mL of a 13% solution of trimethylamine in tetrahydrofuran (1.16 g, 19.7 mmol). The solution is stirred under air at room temperature. 4-(Chloromethyl)benzonitrile (2.70 g, 17.8 mmol) is added in quick portions and the reaction is heated to 60° C. for 2 hours. The reaction is then cooled to room temperature and white precipitates are collected by suction filtration and washed with additional tetrahydrofuran. About 2.80 g of white fluffy powder is collected (75% yield), and the desired product structure is confirmed by ¹H NMR. The partial dendrite suppressive effect of this additive is shown in FIG. 8. This additive strongly suppresses hydrogen evolution.

40 4-(Trimethylammoniummethyl)Anisole Chloride Preparation and Performance.

To a 100 mL flask is added 20 mL of a 13% solution of trimethylamine in tetrahydrofuran (2.32 g, 39.4 mmol) and this is stirred under air at room temperature. (4-Methoxybenzyl)chloride (5.59 g, 4.84 mL, 35.7 mmol) is added in quick portions and the reaction is heated to 60° C. for 3 hours. The reaction is then cooled to room temperature and white precipitates are collected by suction filtration and washed with additional tetrahydrofuran. About 7.08 g of white fluffy powder is collected (92% yield) and the desired product structure is confirmed by ¹H NMR. The dendrite suppressive effect of this additive is shown in FIGS. 9-11. Dendrite suppression is complete under the test conditions at 1 wt % and 0.5 wt %, and partial at 0.1 wt %. Hydrogen evolution is fully suppressed at 1.0 wt % and partially suppressed at 0.5 wt % and 0.01 wt %.

45 An analogous method is used to synthesize 3-(trimethylammoniummethyl)anisole chloride, as well as similar

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4-(trimethylammoniummethyl)-1,2,6-trimethoxybenzene. FIG. 12 shows that 4-(trimethylammoniummethyl)-1,2,6-trimethoxybenzene fully suppresses dendrite formation under the test conditions at 1.0 wt %, and partially suppresses hydrogen evolution. FIG. 22 shows that 3-(trimethylammoniummethyl)anisole chloride fully suppresses hydrogen evolution and dendrite formation.

(4-Methylbenzyl)Trimethylammonium Chloride Preparation and Performance.

To a 100 mL flask is added 10 mL of a 13% solution of trimethylamine in tetrahydrofuran (1.16 g, 19.7 mmol). The solution is stirred under air at room temperature. 4-Methylbenzyl chloride (2.75 g, 2.6 ml, 19.5 mmol) is added in quick portions and the reaction is heated to 60° C. for 3 hours. The reaction is then cooled to room temperature and white precipitates are collected by suction filtration and washed with additional tetrahydrofuran. About 2.92 g of white fluffy powder is collected (75% yield) and the desired product structure is confirmed by ¹H NMR. FIG. 13 shows that 1 wt % (4-methylbenzyl)trimethylammonium chloride fully suppresses dendrite formation under the test conditions, and partially suppresses hydrogen evolution. FIG. 30 shows that 15 wt % (4-methylbenzyl)trimethylammonium chloride fully suppresses dendrite formation and hydrogen evolution under the test conditions. FIG. 31 shows that 0.1 wt % (4-methylbenzyl)trimethylammonium chloride partially suppresses dendrite formation, and less effective in suppressing hydrogen evolution than higher tested concentrations of this additive.

(3,4-Dimethylbenzyl)Trimethylammonium Chloride Preparation and Performance.

To a 100 mL flask is added 10.0 ml of a 13% solution of trimethylamine in tetrahydrofuran (1.16 g, 19.6 mmol). The solution is stirred under air at room temperature. 3,4-Dimethylbenzyl chloride (2.75 g, 17.8 mmol) is added in quick portions and the reaction is heated to 60° C. for 4 hrs. The reaction is then cooled to room temperature and white precipitates are collected by suction filtration and washed with additional tetrahydrofuran. About 2.75 g of white fluffy powder are collected (73% yield) and the desired product structure is confirmed by ¹H NMR as shown in FIG. 27. Also shown in FIG. 27 is an inlay photo showing that 1.0 wt % (3,4-dimethylbenzyl)trimethylammonium chloride fully suppresses dendrite formation and fully suppresses hydrogen evolution under the test conditions.

An analogous method is used to synthesize other isomers of this product, namely, (2-methylbenzyl)trimethylammonium chloride and (3-methylbenzyl)trimethylammonium chloride, as well as (2,4-dimethylbenzyl)trimethylammonium chloride, (2,5-dimethylbenzyl)trimethylammonium chloride, (2,6-dimethylbenzyl)trimethylammonium chloride, (3,5-dimethylbenzyl)trimethylammonium chloride, and (2,4,6-trimethylbenzyl)trimethylammonium chloride. FIG. 14 shows that 1 wt % (2-methylbenzyl)trimethylammonium chloride fully suppresses dendrite formation, and partially suppresses hydrogen evolution. FIG. 20 shows that 1 wt % (3-methylbenzyl)trimethylammonium chloride partially suppresses dendrite formation, and partially suppresses hydrogen evolution, under the test conditions.

(4-Chlorobenzyl)Trimethylammonium Chloride Preparation and Performance.

To a 100 mL flask is added 10 mL of a 13% solution of trimethylamine in tetrahydrofuran (1.16 g, 19.7 mmol). The solution is stirred under air at room temperature. 4-Chlorobenzyl chloride (2.86 g, 17.8 mmol) is added in quick portions and the reaction is heated to 60° C. for 3 hours. The reaction is then cooled to room temperature and the white

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precipitates are collected by suction filtration and washed with additional tetrahydrofuran. About 3.17 g of white fluffy powder are collected (82% yield) and the desired product structure is confirmed by ¹H NMR. FIG. 15 shows that 1 wt % (4-chlorobenzyl)trimethylammonium chloride partially suppresses dendrite formation, and hydrogen evolution, under the test conditions.

An analogous method is used to synthesize (2-chlorobenzyl)trimethylammonium chloride, (3-chlorobenzyl)trimethylammonium chloride, (2-bromobenzyl)trimethylammonium bromide, (3-bromobenzyl)trimethylammonium bromide, and (4-bromobenzyl)trimethylammonium bromide, with the later three using reagent bromobenzyl bromide in place of chlorobenzyl chloride. Similarly, iodobenzyl chlorides are used in an analogous method to produce (2-iodobenzyl)trimethylammonium chloride, (3-iodobenzyl)trimethylammonium chloride, and (4-iodobenzyl)trimethylammonium chloride. FIG. 16 shows that (2-chlorobenzyl)trimethylammonium chloride does not suppress dendrite formation under the test conditions, but does partially suppress hydrogen evolution. FIG. 17 shows that 1 wt % (4-bromobenzyl)trimethylammonium bromide fully suppresses dendrite formation under the test conditions, and partially suppress hydrogen evolution.

Benzyltrimethylphosphonium chloride preparation and performance.

To a 100 mL flask is added 10 mL of a 1M solution of trimethylphosphine in tetrahydrofuran (1.52 g, 20. ml, 20 mmol). The solution is stirred under nitrogen at room temperature. Benzylchloride (2.52 g, 2.3 ml, 20.0 mmol) is added in quick portions and the reaction is heated to 60° C. for 3 hours. The reaction is then cooled to room temperature and white precipitates are collected by brief suction filtration. About 1.80 g of white fluffy powder is collected (44% yield) and the desired product structure is confirmed by ¹H NMR. FIG. 18 shows that 1 wt % benzyltrimethylphosphonium chloride partially suppresses dendrite formation, but does not suppress hydrogen evolution, under the test conditions.

(2-Hydroxybenzyl)Trimethylammonium Iodide Preparation and Performance.

To a 100 mL flask is added 2-[(Dimethylamino)methyl] phenol (2.45 g, 16.2 mmol) and tetrahydrofuran (25 mL). The clear solution is cooled to 0° C. by an ice bath under air and with magnetic stirring. To this solution iodomethane (3.45 g, 24.3 mmol) is added dropwise. After stirring for 20 minutes the ice bath is removed and the reaction proceeds at room temperature for 3 hours as a viscous oil forms at the bottom of the flask. The solvents are removed from the reaction by reduced pressure (Rotavap) to a mass of orange/brown amorphous solid measuring 4.6 g (94% yield). The desired product structure is confirmed by ¹H NMR. FIG. 19 shows that 1 wt % (2-hydroxybenzyl)trimethylammonium iodide partially suppresses dendrite formation, and partially suppresses hydrogen evolution, under the test conditions.

4-(Trimethylammoniummethyl)Benzoic Acid Bromide Preparation.

To a 100 mL flask is added 8.0 mL of a 13% solution of trimethylamine in tetrahydrofuran (0.92 g, 15.6 mmol) is diluted in 30 mL acetonitrile. The solution is stirred under air at room temperature. Then, 4-(bromomethyl)benzoic Acid (3.36 g, 15.6 mmol) is added in quick portions and the reaction is heated to 80° C. for 3 hrs. The reaction is then cooled to room temperature and white precipitates are collected by suction filtration and washed with additional tetrahydrofuran. About 4.10 g of white solids are collected (95.6% yield) and the desired product structure is confirmed

by ^1H NMR. FIG. 21 shows that 1 wt % 4-(Trimethylammoniummethyl)benzoic acid bromide partially suppresses dendrite formation, and partially suppresses hydrogen evolution, under the test conditions.

(2,6-Dimethylbenzyl)Trimethylammonium Chloride Preparation.

To a 100 mL flask is added 9.1 mL of a 13% solution of trimethylamine in tetrahydrofuran (1.05 g, 17.8 mmol). The solution is stirred under air at room temperature. 2,6-Dimethylbenzyl chloride (2.5 g, 16.2 mmol) is added in quick portions and the reaction is heated to 60° C. for 3 hrs. The reaction is then cooled to room temperature and the white precipitates are collected by suction filtration and washed with additional tetrahydrofuran. About 3.05 g of white fluffy powder are collected (88% yield) and the desired product structure is confirmed by ^1H NMR. FIG. 24 shows that 1.0 wt % (2,6-Dimethylbenzyl)trimethylammonium chloride partially suppresses dendrite formation, but does not suppress hydrogen evolution, under the test conditions.

FIG. 23 shows that 1.0 wt % Benzalkonium Chloride is effective in fully suppressing dendrite formation and hydrogen evolution under the test condition. The tested additive is a mixture having the following formula, where $\text{R}^5 = \text{C}_n\text{H}_{2n+1}$ where $8 \leq n \leq 18$:

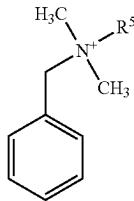
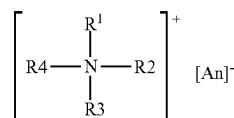


FIG. 32 shows a schematic view of a zinc-battery cell 100. The cell includes a zinc anode 102 in communication with a cathode 108 through an electrolyte 104. A porous separator 110 such as a membrane may be interposed between the cathode 108 and the electrolyte 104. The person having ordinary skill in the art will readily appreciate that the cathode may comprise a wide variety of known materials such as without limitation, air, carbon, nickel, manganese, silver, iron, lithium vanadium, cerium, bromine, chlorine. More specifically, cathodes of the present invention include MnO_2 , Mn_2O_3 , V_2O_5 , VO_2 , LiV_3O_8 . Cathodes according to embodiments of the invention also include hexacyanoferates (HCFs) also known as Prussian blue analogs (PBAs) including $\text{Mn}[\text{Fe}(\text{CN})_6]$, $\text{Fe}[\text{Fe}(\text{CN})_6]$, $\text{Co}[\text{Fe}(\text{CN})_6]$, $\text{Ni}[\text{Fe}(\text{CN})_6]$, $\text{Cu}[\text{Fe}(\text{CN})_6]$, and $\text{Zn}[\text{Fe}(\text{CN})_6]$.

It will be apparent to those skilled in the art that the above methods and apparatuses may be changed or modified without departing from the general scope of the invention. The invention is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

I claim:

1. A zinc battery cell, comprising:
a cathode in electric communication with a zinc anode through an aqueous electrolyte, wherein the cathode is selected from one or more of carbon, air, nickel, manganese, silver, iron, lithium vanadium, cerium, bromine, chlorine, MnO_2 , Mn_2O_3 , V_2O_5 , VO_2 , LiV_3O_8 , $\text{Mn}[\text{Fe}(\text{CN})_6]$, $\text{Fe}[\text{Fe}(\text{CN})_6]$, $\text{Co}[\text{Fe}(\text{CN})_6]$, $\text{Ni}[\text{Fe}(\text{CN})_6]$, $\text{Cu}[\text{Fe}(\text{CN})_6]$, and $\text{Zn}[\text{Fe}(\text{CN})_6]$;
wherein the electrolyte comprises an amount of an electrolyte additive effective for use in reducing dendrite formation and hydrogen evolution in an amount of greater than 0 wt % to less than 25 wt %, comprising:



wherein, N is a central nitrogen atom having a +1 charge; wherein R1 is selected from the group consisting of 4-methylene-toluene, 3-methylene-toluene, 2-methylene-toluene, 4-methylene-chlorobenzene, 3-methylene-chlorobenzene, 2-methylene-chlorobenzene, 4-methylene-bromobenzene, 3-methylene-bromobenzene, 2-methylene-bromobenzene, 4-methylene-iodobenzene, 3-methylene-iodobenzene, 2-methylene-iodobenzene, 4-methylene-cyanobenzene, 3-methylene-cyanobenzene, 2-methylene-cyanobenzene, 4-methylene-anisole, 3-methylene-anisole, 2-methylene-anisole, 1-methylnaphthalene, 1-methylene-2,6-dimethylbenzene, 1-methylene-2,4-dimethylbenzene, 1-methylene-3,4-dimethylbenzene, 1-methylene-2,5-dimethylbenzene, 1-methylene-3,5-dimethylbenzene, 1-methylene-2,4,6-trimethylbenzene, 1-methylene-3,4,5-trimethoxybenzene, 1-methylene-2,6-dichlorobenzene, 4-methylene-nitrobenzene, 4-methylene-benzoic acid, 3-methylene-benzoic acid, 2-methylene-benzoic acid, 2-methylene-phenol, 3-methylene-phenol, and 4-methylene-phenol;

wherein R2, R3, and R4 are independently selected from R1, or a linear or non-linear alkyl group from C1 to C25; and,
wherein $[\text{An}]^-$ is a counter anion.

2. The zinc battery of claim 1, wherein the counter anion is selected from chloride, bromide, iodide, fluoride, hydroxide, nitrate, nitrite, sulphate, sulphite, phosphate, perchlorate, or any combination thereof.

3. The zinc battery of claim 1, wherein R2, R3, and R4 are independently selected from methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-octyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, or n-octadecyl.

* * * * *