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United States Patent

Kind Code

B2

Date of Patent

Inventor(s)

12382984

August 12, 2025

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Use of pectin or other anionic polymers in the stabilization and controlled release of nicotine in oral sensorial tobacco products or nicotine containing non-tobacco oral sensorial products

### **Abstract**

The use of pectins and/or polymers to prevent nicotine oxidation in tobacco containing products is disclosed. These polymers may be naturally occurring anionic polymers or synthetic polymers. These pectins and/or polymers prevent nicotine from oxidizing into cotinine, nicotine-cis-N-oxide, nicotine-trans-N-oxide, and/or nicotine-1,1-di-N-oxide. Molluscicides, algaecides, pesticides, and stabilized nicotine compositions comprising nicotine and pectin, anionic polymers, or combinations thereof are disclosed.

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Appl. No.: 18/431283

Filed: February 02, 2024

# **Prior Publication Data**

**Document Identifier**US 20240172787 A1

Publication Date
May. 30, 2024

**Related U.S. Application Data** 

continuation parent-doc US 17130542 20201222 US 11925201 child-doc US 18431283 continuation parent-doc US 16194787 20181119 US 10881134 20210105 child-doc US 17130542 continuation parent-doc US 14206515 20140312 US 10130120 20181120 child-doc US 16194787 us-provisional-application US 61799428 20130315

# **Publication Classification**

Int. Cl.: A24B15/40 (20060101); A24B13/00 (20060101); A24B15/30 (20060101)

**U.S. Cl.:** 

CPC **A24B15/403** (20130101); **A24B13/00** (20130101); **A24B15/30** (20130101); **A24B15/301** 

(20130101); **A24B15/302** (20130101);

# **Field of Classification Search**

**USPC:** None

# **References Cited**

## **U.S. PATENT DOCUMENTS**

U.S. TATENT DUC	OWILIVIO			
Patent No.	<b>Issued Date</b>	<b>Patentee Name</b>	U.S. Cl.	CPC
3746012	12/1972	Deszyck	N/A	N/A
3861400	12/1974	Perkins et al.	N/A	N/A
4142535	12/1978	Perkins et al.	N/A	N/A
4674519	12/1986	Keritsis et al.	N/A	N/A
5525351	12/1995	Dam	N/A	N/A
5567462	12/1995	Ehrlich	N/A	N/A
5935604	12/1998	Illum	N/A	N/A
6110495	12/1999	Dam	N/A	N/A
6432440	12/2001	Watts et al.	N/A	N/A
6607752	12/2002	Bellamy et al.	N/A	N/A
8042552	12/2010	Xue et al.	N/A	N/A
8733369	12/2013	Rees et al.	N/A	N/A
10881134	12/2020	Mishra et al.	N/A	N/A
2004/0194793	12/2003	Lindell	N/A	N/A
2006/0147498	12/2005	Jonsson et al.	N/A	N/A
2006/0275344	12/2005	Mody et al.	N/A	N/A
2008/0286340	12/2007	Andersson et al.	N/A	N/A
2009/0092573	12/2008	Andersen	N/A	N/A
2009/0293895	12/2008	Axelsson et al.	N/A	N/A
2010/0086981	12/2009	LaTouf et al.	N/A	N/A
2010/0130562	12/2009	Hite et al.	N/A	N/A
2010/0247582	12/2009	Sorensen et al.	N/A	N/A
2010/0247586	12/2009	Hugerth et al.	N/A	N/A
2010/0303969	12/2009	Sengupta et al.	N/A	N/A
2011/0071184	12/2010	Bunick	N/A	N/A
2011/0083681	12/2010	Sengupta et al.	N/A	N/A

2012/0048285	12/2011	Mishra et al.	N/A	N/A
2012/0052021	12/2011	Kobal et al.	N/A	N/A
2012/0128734	12/2011	Hubinette et al.	N/A	N/A
2012/0247492	12/2011	Kobal et al.	N/A	N/A
2013/0125904	12/2012	Chen et al.	N/A	N/A
2013/0192620	12/2012	Tucker et al.	N/A	N/A

#### FOREIGN PATENT DOCUMENTS

Patent No.	<b>Application Date</b>	Country	CPC
1495941	12/1976	GB	N/A
WO-2010104464	12/2009	WO	N/A

#### OTHER PUBLICATIONS

Definition of "complex", IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"), 1997, [online], [retrieved on Jun. 24, 2014], Retrieved from the Internet: <URL: http://goldbook.iupac.org (2006-)>. (Year: 2006). cited by examiner

Polysacharrides (Sugars, Gums) Used in Cosmetics, Making Cosmetics Inc., no date, [online], retrieved from the Internet, [retrieved Apr. 4, 2015],

<URL:http://www.makingcosmetics.com/articles/20-polysaccharides-sugars--gums-in-cosmetics.pdf>. cited by applicant

Definition of complex, Chemistry Dictionary, no date, [online], retrieved from the Internet, [retrieved Apr. 4, 2015], <URL:http://www.chemicool.com/definition/complex.html>. cited by applicant

Definition of "complex", IUPAC Gold Book, 1994, [online], retrieved from the Internet, retrieved Jun. 24, 2014], <URL:http://goldbook.iupac.org/C01203.html>. cited by applicant International Search Report dated Jun. 26, 2014, for International Patent Publication No. PCT/US2014/025931. cited by applicant

Definition of "complex", IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"), 1997, [online], [retrieved on Jun. 24, 2014], Retrieved from the Internet: <URL:http://goldbook.iupac.org (2006-)>. (Year: 1997). cited by applicant

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# **Background/Summary**

CROSS-REFERENCE TO RELATED APPLICATIONS (1) This application is a continuation application of U.S. patent application Ser. No. 17/130,542, filed on Dec. 22, 2020, which is a continuation application of U.S. patent application Ser. No. 16/194,787, filed on Nov. 19, 2018, which is a continuation application of U.S. patent application Ser. No. 14/206,515, filed on Mar. 12, 2014, now U.S. Pat. No. 10,130,120, issued on Nov. 20, 2018, which claims priority to U.S. Provisional Patent Application Ser. No. 61/799,428, filed on Mar. 15, 2013, the entire contents of each of which are incorporated herein by reference thereto.

#### BACKGROUND

(1) Nicotine is a well-known and highly characterized naturally occurring alkaloid found in the tobacco plant, *Nicotiana tabacum*. Under ambient conditions, nicotine is an oily, volatile, hygroscopic liquid that is sensitive to light and air. Due to its volatility, nicotine may evaporate during its processing. Additionally, the nitrogen in the pyrrolidinic ring can undergo protonation in

- the presence of an acid. Further, any nicotine free base present in an article is susceptible to oxidation through an electrophilic attack.
- (2) Thus, the stabilization of nicotine in oral sensorial tobacco products, or nicotine containing non-tobacco oral sensorial products, is desirable.

## **SUMMARY**

- (3) The present disclosure is related to the use of pectins and/or polymers to prevent nicotine oxidation in tobacco containing products. In one embodiment, the use of pectins and/or polymers to prevent nicotine oxidation in tobacco containing products, wherein said polymers are naturally occurring anionoic polymers is disclosed. In another embodiment, the use of pectins and/or polymers are synthetic polymers is disclosed. In another embodiment, the use of pectins and/or polymers to prevent nicotine oxidation in tobacco containing products, wherein nicotine is prevented from oxidizing into cotinine, nicotine-cis-N-oxide, nicotine-trans-N-oxide, and/or nicotine-1,1-di-N-oxide is disclosed. In another embodiment, a method of preventing nicotine oxidation in tobacco containing products comprising mixing the tobacco with pectins and/or polymers is disclosed.
- (4) One embodiment is a process for preventing nicotine oxidation in tobacco containing products comprising pectin and/or anionic polymers, which can form salts with protonated forms of nicotine that are typically present below pH levels of around 9 or so, can act like an ion-exchange resin and hold nicotine in close proximity by electrostatic attraction.
- (5) Another embodiment is a method for stabilizing nicotine comprising employing pectin and/or an anionic polymer at a pH of around 6 (above pH values of about 4 or so and below pH levels of about 9).
- (6) Another embodiment is a method for reducing the formation of oxidation products from nicotine comprising employing pectin and/or an anionic polymer.
- (7) Another embodiment is a molluscicide composition comprising nicotine and pectin, an anionic polymer, or a combination thereof, wherein said pectin, an anionic polymer, or a combination thereof stabilizes said nicotine.
- (8) Another embodiment is an algaecide composition comprising nicotine, and pectin, an anionic polymer, or a combination thereof, wherein said pectin, an anionic polymer, or a combination thereof stabilizes said nicotine.
- (9) Another embodiment is a pesticide composition comprising nicotine, and pectin, an anionic polymer, or a combination thereof, wherein said pectin, an anionic polymer, or a combination thereof stabilizes said nicotine.
- (10) Another embodiment is a stabilized nicotine composition comprising nicotine, and pectin, an anionic polymer, or a combination thereof, wherein the pH of said composition is above pH values of about 4 or so and below pH levels of about 9.
- (11) A further embodiment is a controlled-release nicotine composition comprising nicotine, and further comprising pectin, an ionic polymer, or a combination thereof.
- (12) Another embodiment is a method for controlling the release of nicotine comprising complexing nicotine with a pectin, an anionic polymer, or a combination thereof at a pH of above pH values of about 4 or so and below pH levels of about 9.
- (13) A further embodiment is a controlled-release nicotine article comprising pectin, an anionic polymer, or a combination thereof. Further envisioned is a controlled-release nicotine article comprising pectin, an anionic polymer, or a combination thereof, wherein the article is a lit-end cigarette, an electrically heated cigarette, chewing tobacco, snus, dry snuff, moist snuff, tablets, sticks, strips, pouched products, chewable gum, or a wrapper.

## **DETAILED DESCRIPTION**

- (1) Nicotine, or 3-[(2S)-1-methylpyrrolidin-2-yl]pyridine, is a tertiary amine with the following structure:
- (2) ##STR00001##

Nicotine constitutes approximately 0.6-3.0% of the dry weight of tobacco. Nicotine has numerous commercial uses including as a fumigant, an insecticide, and in smoking articles such as cigarettes, cigars, and in pipes and smokeless tobacco products such as chewing tobacco, snuff, pouches and gum. It is well known that nicotine oxidation is catalyzed by light and that nicotine is more stable in its protonated form. In nicotine chewing gum products (pharmaceutical products designed for smoking cessation therapy) the nicotine can be bound to the weak cation-exchanger polyacrilex to prevent oxidation.

- (3) It is desirable to prevent the oxidation of the nicotine in smoking articles and smokeless tobacco products. A common method to reduce the processing and stability issues associated with the nicotine compound involves the preparation of a complex of nicotine and an ion exchange resin. Nicotine ion exchange complexes are described in U.S. Pat. Nos. 5,935,604 and 6,607,752 and U.S. Pat. App. Pub. Nos. 2009/0092573 and 2010/0130562.
- (4) Ion exchange resins are characterized by their capacity to exchange ions. The ion exchange capacity is measured as the number of equivalents of an ion that can be exchanged and can be expressed with reference to the mass of the polymer or its volume. Ion exchange resins are known in the art and can be manufactured in forms such as spherical and non-spherical particles with size in the range of 0.001 mm to 2 mm.
- (5) Pectins are natural polymers related to carbohydrates, except that C-6 contains a fully oxidized carboxylic acid (or corresponding methyl ester or carboxamide) group instead of a hydroxymethyl group. The principal subunit is known as galacturonic acid, which can be copolymerized with L-rhamnose. Other sugars are featured as side-chain substituents. The carboxylic acid form, more particularly the carboxylate anionic form present at pH values above about 4 or so, forms "salts" with protonated forms of nicotine that are typically present below pH levels of around 9 or so.
- (6) Provided herein is the use of pectins combined with nicotine or nicotine-containing tobacco extracts to create reconstituted tobaccos or other nicotine-containing materials that can be used in an oral sensorial (including chewable) product. Chewable products include chewing tobacco, snus, dry snuff, moist snuff, tablets, sticks, strips, pouched products, chewable gum, spongy material, or combination of these.
- (7) An embodiment is the use of pectins and/or polymers to prevent nicotine oxidation in tobacco containing products. These polymers may be naturally occurring anionic polymers or synthetic polymers. Described herein is a use wherein nicotine is prevented from oxidizing into cotinine, nicotine-cis-N-oxide, nicotine-trans-N-oxide, and/or nicotine-1,1-di-N-oxide.
- (8) Also described is the use of pectin to allow greater recovery of nicotine from tobaccoprocessing streams involved in reconstituted-leaf production for lit-end cigarettes and electrically heated cigarettes. If the more soluble versions of anionic pectins are used and ingested, they will continue to bind nicotine.
- (9) If the pectin used has low water-solubility, the pectin, within the appropriate pH range, can act like an "ion-exchange resin," and hold nicotine in close proximity by electrostatic attraction that is characteristic of ionized salts. Natural tobacco pectins attract nicotine at pH levels of around 6, which can prolong the release of nicotine when such tobaccos are chewed or otherwise exposed to saliva in the mouth.
- (10) Pectin may be extracted from tobacco, but also commercially available pectin isolated from sources such as apple pomace, citrus peels, sugarbeet waste from sugar manufacturing, sunflower heads discarded from seed harvesting, mango waste, and other commercially available pectins may be used.

- (11) Physical properties of several types of pectin suitable for use herein are provided in Table 1.
- (12) TABLE-US-00001 TABLE 1 PHYSICAL PROPERTY DATA FOR PECTINS Intrinsic viscosity Huggins Solvent Pectin Description (dl/g) coefficient conditions pH MW Sigma 6% ester, 5.8556 0.0643 Good 3.389 613,740 apple low ester draining pectin pectin Genu Amidated 4.9261 0.8462 Poor 2.984 479,760 Pectin low ester solvent Type pectin, 17% conditions X-916-02 amidation, 34% ester, no sugar Genu Around 3.6156 0.827 Poor, non- 3.052 376,300 Pectin 40% ester draining Type LM pectin, no 18-CG-Z sugar Tobacco Very low 1.881 0.4154 Very 2.983 259,530 pectin ester good (unwashed) pectin draining Tobacco Very low 1.3514 0.02749 Very 4.420 237,270 pectin ester good (dialyzed) pectin draining
- (13) Other naturally occurring anionic polymers, or synthetic anionic polymers that have achieved GRAS status for use in foods or cosmetics, may also be used. Such polymers include carboxymethylcellulose, other carboxylated carbohydrate-derived polymers such as alginate or alginic acid, sulfated carbohydrate polymers such as carrageenan, fucoidans, heparan sulfate or heparin, and phosphorylated polymers such as deoxyribonucleic acid (DNA) or ribonucleic acid (RNA). All of these exhibit ion-exchange characteristics with respect to nicotine, within an appropriate pH range. The sulfated or phosphorylated polymers have a lower effective pH range than the carboxylate-containing polymers, due to their inherently lower pKa values, subject to chemical stability impairments that may occur under excessively acidic conditions.
- (14) Another embodiment is the use of pectins combined with nicotine or nicotine-containing tobacco extracts to create nicotine releasing wrappers of oral sensorial (including chewable) products.
- (15) The examples explained below are given by way of illustration only and should not be interpreted as constituting any limitation of the subject of the present invention.

## **EXAMPLES**

Example 1

- (16) Nicotine and pectin compositions may be formed by mixing nicotine (about 1%—about 30%) with pectin or anionic polymer combinations (about 70%—about 99%).
- (17) While the foregoing describes in detail the use of pectin or other anionic polymers in the stabilization of nicotine in oral sensorial tobacco products or nicotine containing non-tobacco oral sensorial products with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications equivalents to the use of pectin or other anionic polymers in the stabilization of nicotine in oral sensorial tobacco products or nicotine containing non-tobacco oral sensorial products may be employed, which do not materially depart from the spirit and scope. Accordingly, all such changes, modifications, and equivalents that fall within the spirit and scope as defined by the appended claims are intended to be encompassed thereby. (18) All publications cited herein are incorporated by reference in their entireties for all purposes.

## **Claims**

- 1. A pouched product comprising: reconstituted tobacco; and a mixture including, nicotine in an amount ranging from 1 weight percent to 30 weight percent, and a stabilizing composition in an amount ranging from 70 weight percent to 90 weight percent, the stabilizing composition including, pectin, a carboxylated polymer, a sulfated polymer, a phosphorylated polymer, or any combination thereof.
- 2. The pouched product of claim 1, further comprising: a tobacco extract, the tobacco extract including, the nicotine.
- 3. The pouched product of claim 1, wherein the nicotine and the stabilizing composition are in the form of a complex.
- 4. The pouched product of claim 1, wherein the stabilizing composition includes the pectin.
- 5. The pouched product of claim 4, wherein the pectin is electrostatically attracted to the nicotine.

- 6. The pouched product of claim 4, wherein the pectin includes tobacco pectin.
- 7. The pouched product of claim 6, wherein the tobacco pectin is configured to prolong release of the nicotine from the pouched product during exposure to saliva.
- 8. The pouched product of claim 6, wherein the tobacco pectin includes unwashed tobacco pectin.
- 9. The pouched product of claim 6, wherein the tobacco pectin includes dialyzed tobacco pectin.
- 10. The pouched product of claim 4, wherein the pectin includes apple-derived pectin, citrus-derived pectin, sugar beet-derived pectin, sunflower-derived pectin, mango-derived pectin, or any combination thereof.
- 11. The pouched product of claim 1, wherein the stabilizing composition includes the carboxylated polymer, and the carboxylated polymer includes carboxymethylcellulose, alginate, alginic acid, or any combination thereof.
- 12. The pouched product of claim 1, wherein the stabilizing composition includes the sulfated polymer, and the sulfated polymer includes carrageenan, fucoidan, heparan sulfate, heparin, or any combination thereof.
- 13. The pouched product of claim 1, wherein the stabilizing composition includes the phosphorylated polymer, and the phosphorylated polymer includes deoxyribonucleic acid (DNA), ribonucleic acid (RNA), or both DNA and RNA.
- 14. The pouched product of claim 1, wherein the stabilizing composition is configured to reduce oxidation of the nicotine into cotinine, nicotine-cis-N-oxide, nicotine-trans-N-oxide, nicotine-1,1-di-N-oxide, or any combination thereof.
- 15. A pouched product comprising: a wrapper; and a releasable composition on the wrapper, the releasable composition including, nicotine in an amount ranging from 1 weight percent to 30 weight percent of the releasable composition, and a stabilizing composition in an amount ranging from 70 weight percent to 99 weight percent of the releasable composition, the releasable composition including, pectin, a carboxylated carbohydrate polymer, a sulfated polymer, a phosphorylated polymer, or any combination thereof.
- 16. The pouched product of claim 15, wherein the stabilizing composition includes the pectin.
- 17. The pouched product of claim 15, wherein the pectin includes tobacco pectin.
- 18. The pouched product of claim 15, wherein the pectin includes unwashed tobacco pectin, dialyzed tobacco pectin, or both unwashed tobacco pectin and dialyzed tobacco pectin.
- 19. A pouched product comprising: nicotine in an amount ranging from 1 weight percent to 30 weight percent, and a stabilizing composition in an amount ranging from 70 weight percent to 90 weight percent, the stabilizing composition including, a sulfated polymer including deoxyribonucleic acid (DNA), ribonucleic acid (RNA), or both DNA and RNA.