

US012382984B2

(12) United States Patent

Mishra et al.

(10) Patent No.: US 12,382,984 B2

(45) **Date of Patent:** *Aug. 12, 2025

(54) 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

(71) Applicant: Altria Client Services LLC, Richmond, VA (US)

(72) Inventors: Munmaya K. Mishra, Manakin Sabot, VA (US); Jason Flora, Richmond, VA (US); Georgios D. Karles, Richmond, VA (US); Christophe Claude Galopin, Chesterfield, VA (US); Diane Gee,

Chesterfield, VA (US); John B. Paine, III, Midlothian, VA (US); Douglas Antonio Fernandez, Richmond, VA (US)

(73) Assignee: Altria Client Services LLC,

Richmond, VA (US)

(*) Notice: Subject to any disclaimer, the term of this

patent is extended or adjusted under 35

U.S.C. 154(b) by 0 days.

This patent is subject to a terminal dis-

claimer.

(21) Appl. No.: 18/431,283

(22) Filed: Feb. 2, 2024

(65) Prior Publication Data

US 2024/0172787 A1 May 30, 2024

Related U.S. Application Data

- (63) Continuation of application No. 17/130,542, filed on Dec. 22, 2020, now Pat. No. 11,925,201, which is a continuation of application No. 16/194,787, filed on Nov. 19, 2018, now Pat. No. 10,881,134, which is a continuation of application No. 14/206,515, filed on Mar. 12, 2014, now Pat. No. 10,130,120.
- (60) Provisional application No. 61/799,428, filed on Mar. 15, 2013.

(51) Int. Cl. A24B 15/40 (2006.01) A24B 13/00 (2006.01) A24B 15/30 (2006.01)

(52) U.S. Cl.

(58) Field of Classification Search

None See application file for complete search history.

(56) References Cited

U.S. PATENT DOCUMENTS

3,746,012 A	7/1973	Deszyck					
3,861,400 A	1/1975	Perkins et al.					
4,142,535 A	3/1979	Perkins et al.					
4,674,519 A	6/1987	Keritsis et al.					
5,525,351 A	6/1996	Dam					
5,567,462 A	10/1996	Ehrlich					
5,935,604 A	8/1999	Illum					
6,110,495 A	8/2000	Dam					
6,432,440 B1	8/2002	Watts et al.					
6,607,752 B2	8/2003	Bellamy et al.					
8,042,552 B2	10/2011	Xue et al.					
8,733,369 B2	5/2014	Rees et al.					
10,881,134 B2	1/2021	Mishra et al.					
2004/0194793 A1	10/2004	Lindell					
2006/0147498 A1	7/2006	Jonsson et al.					
2006/0275344 A1	12/2006	Mody et al.					
2008/0286340 A1	11/2008	Andersson et al.					
2009/0092573 A1	4/2009	Andersen					
2009/0293895 A1	12/2009	Axelsson et al.					
2010/0086981 A1	4/2010	LaTouf et al.					
2010/0130562 A1	5/2010	Hite et al.					
2010/0247582 A1	9/2010	Sorensen et al.					
2010/0247586 A1	9/2010	Hugerth et al.					
2010/0303969 A1	12/2010	Sengupta et al.					
2011/0071184 A1	3/2011	Bunick					
2011/0083681 A1	4/2011	Sengupta et al.					
2012/0048285 A1	3/2012	Mishra et al.					
2012/0052021 A1	3/2012	Kobal et al.					
	(Con	(Continued)					
	(Commaca)						

FOREIGN PATENT DOCUMENTS

GB 1495941 A 12/1977 WO WO-2010104464 A1 9/2010

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).*

(Continued)

Primary Examiner — Dennis R Cordray (74) Attorney, Agent, or Firm — Harness, Dickey & Pierce, P.L.C.

(57) 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.

19 Claims, No Drawings

(56) References Cited

U.S. PATENT DOCUMENTS

 2012/0128734
 A1
 5/2012
 Hubinette et al.

 2012/0247492
 A1
 10/2012
 Kobal et al.

 2013/0125904
 A1
 5/2013
 Chen et al.

 2013/0192620
 A1
 8/2013
 Tucker et al.

OTHER PUBLICATIONS

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>.

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

Definition of "complex", IUPAC Gold Book, 1994, [online], retrieved from the Internet, retrieved Jun. 24, 2014], <URL:http://goldbook.iupac.org/C01203.html>.

International Search Report dated Jun. 26, 2014, for International Patent Publication No. PCT/US2014/025931.

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 examiner

1

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

CROSS-REFERENCE TO RELATED APPLICATIONS

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 20 each of which are incorporated herein by reference thereto.

BACKGROUND

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.

Thus, the stabilization of nicotine in oral sensorial tobacco products, or nicotine containing non-tobacco oral ³⁵ sensorial products, is desirable.

SUMMARY

The present disclosure is related to the use of pectins 40 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 45 embodiment, the use of pectins and/or polymers to prevent nicotine oxidation in tobacco containing products, wherein said 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 50 nicotine is prevented from oxidizing into cotinine, nicotinecis-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 55 polymers is disclosed.

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 60 levels of around 9 or so, can act like an ion-exchange resin and hold nicotine in close proximity by electrostatic attraction

Another embodiment is a method for stabilizing nicotine comprising employing pectin and/or an anionic polymer at 65 a pH of around 6 (above pH values of about 4 or so and below pH levels of about 9).

2

Another embodiment is a method for reducing the formation of oxidation products from nicotine comprising employing pectin and/or an anionic polymer.

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.

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.

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.

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.

A further embodiment is a controlled-release nicotine composition comprising nicotine, and further comprising pectin, an ionic polymer, or a combination thereof.

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.

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

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

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.

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.

Ion exchange resins are characterized by their capacity to exchange ions. The ion exchange capacity is measured as the 5 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 nonspherical particles with size in the range of 0.001 mm to 2 10

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 15 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

4

If the pectin used has low water-solubility, the pectin, within the appropriate pH range, can act like an "ionexchange 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.

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

Physical properties of several types of pectin suitable for use herein are provided in Table 1.

TABLE 1

PHYSICAL PROPERTY DATA FOR PECTINS								
Pectin	Description	Intrinsic viscosity (dl/g)	Huggins coefficient	Solvent conditions	pН	MW		
Sigma apple pectin	6% ester, low ester pectin	5.8556	0.0643	Good draining	3.389	613,740		
Genu Pectin Type X-916-02	Amidated low ester pectin, 17% amidation, 34% ester, no sugar	4.9261	0.8462	Poor solvent conditions	2.984	479,760		
Genu Pectin Type LM 18-CG-Z	Around 40% ester pectin, no sugar	3.6156	0.827	Poor, non- draining	3.052	376,300		
Tobacco pectin (unwashed)	Very low ester pectin	1.881	0.4154	Very good draining	2.983	259,530		
Tobacco pectin (dialyzed)	Very low ester pectin	1.3514	0.02749	Very good draining	4.420	237,270		

carboxylate anionic form present at pH values above about are typically present below pH levels of around 9 or so.

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) 50 product. Chewable products include chewing tobacco, snus, dry snuff, moist snuff, tablets, sticks, strips, pouched products, chewable gum, spongy material, or combination of these.

An embodiment is the use of pectins and/or polymers to 55 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 nico- 60 tine-1,1-di-N-oxide.

Also described is the use of pectin to allow greater recovery of nicotine from tobacco-processing streams involved in reconstituted-leaf production for lit-end cigarettes and electrically heated cigarettes. If the more soluble 65 versions of anionic pectins are used and ingested, they will continue to bind nicotine.

Other naturally occurring anionic polymers, or synthetic 4 or so, forms "salts" with protonated forms of nicotine that 45 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.

> 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.

> 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.

Example 1

Nicotine and pectin compositions may be formed by mixing nicotine (about 1%—about 30%) with pectin or anionic polymer combinations (about 70%—about 99%).

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 nontobacco 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 15 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 20 thereby.

All publications cited herein are incorporated by reference in their entireties for all purposes.

What is claimed is:

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
- 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 45 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 50 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

6

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

25

- 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.

* * * * *