



- (51) **International Patent Classification:**
A23L 27/00 (2016.01) *A23L 3/46* (2006.01)
- (21) **International Application Number:**
PCT/EP2016/061798
- (22) **International Filing Date:**
25 May 2016 (25.05.2016)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/166,737 27 May 2015 (27.05.2015) US
- (71) **Applicant:** GIVAUDAN SA [CH/CH]; Chemin de la Parfumerie 5, 1214 Vernier (CH).
- (72) **Inventors:** CHANEY, Michael; 305 Helen Street, Ludlow, Kentucky 41016 (US). SHERMAN, Gregory Alan; 4221 Edinburgh Drive, Cincinnati, Ohio 45245 (US).
- (74) **Agent:** MC STEA, John; Ueberlandstrasse 138, 8600 Dübendorf (CH).
- (81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) **Title:** SPRAY DRYING

(57) **Abstract:** A method of preparing spray-dried flavor-containing particles, comprising the addition of flavor to an aqueous, sugar-free matrix and spray-drying the resulting blend, the matrix comprising an emulsifier, a film former and at least one metal salt, selected from the ferrous, alkali metal and alkaline earth metal salts of citric, gluconic and tartaric acids. The method allows the preparation of highly-stable, oxidation- and moisture resistant flavor particles.



SPRAY DRYING

This disclosure relates to spray drying, and to a product obtained thereby.

- 5 Spray drying is a commonly-used technique in the formulation of flavors. The flavor is blended with an aqueous matrix material, which is then sprayed into a heated atmosphere. This dries and solidifies the sprayed particles, which can then be collected. Typical matrix constituents comprise an emulsifier, a film-former and/or filler and a plasticizer.
- 10 One very commonly used plasticizer is sugar. The function of the plasticizer is to provide low porosity, increased density and increased resistance to oxidation. Sugar performs these tasks admirably. Unfortunately, sugar is also slightly hygroscopic and this reduces the humidity resistance.
- 15 It has now been found that it is possible to reduce considerably, and even eliminate completely, this problem, and to obtain spray-dried particles with excellent humidity resistance, plus all the other desirable properties. There is therefore provided a method of preparing spray-dried flavor-containing particles, comprising the addition of flavor to an aqueous, sugar-free matrix and spray-drying the resulting blend, the matrix comprising an emulsifier, a film former and at least one metal
- 20 salt, selected from the ferrous, alkali metal and alkaline earth metal salts of citric, gluconic and tartaric acids.

There is additionally provided a spray-dried, flavor-containing particle comprising flavor in a sugar-free matrix, the matrix comprising an emulsifier, a film former and at least one metal salt, selected

25 from the ferrous, alkali metal and alkaline earth metal salts of citric, gluconic and tartaric acids.

The matrix may be any of the usual materials known to the art for use in spray-dried flavors. The emulsifier may be selected from any natural material with the desired surface activity. Typical examples include proteins and starches, including modified starches. A particular starch is OSA

30 (octenyl succinate anhydride)-modified starch.

The film-former/filler may be any suitable material, non-limiting examples including food grade and commercially-utilized film formers such as corn syrup solids, gum acacia, modified celluloses, gelatin and other animalic or botanical proteins, a particular example being maltodextrin.

35

The metal salts are well-known and commercially-available items. Particular examples of such salts include, but are not limited to: potassium gluconate, tripotassium citrate, potassium bitartrate, sodium gluconate, magnesium gluconate and ferrous gluconate. A particular example is potassium gluconate.

40

More than one such salt may be used. Particular combinations include:

- tripotassium citrate and potassium gluconate
- tripotassium citrate and potassium bitartrate
- potassium gluconate, tripotassium citrate and potassium bitartrate

5

The salts may be used at a concentration of from 10-30% by weight of the non-flavor particle constituents (that is, all particle constituents minus the flavor). The matrix proportion of the particle is from 10-90%. The flavor is present at a proportion of up to 15% by weight of the particle.

10 Particular individual salt weight proportions of the non-flavor particle constituents include:

Potassium Gluconate	20-30%
Magnesium Gluconate	25%
Ferrous Gluconate	25%
Potassium Bitartrate	25%

15 Tripotassium Citrate 10-25%
 Magnesium Citrate 20-30%

Particular combinations of salts by weight of non-flavor particle constituents:

20 Potassium Gluconate & Tripotassium Citrate (1:2) at 30%
 Potassium Gluconate & Magnesium Citrate (1:2) at 30%
 Potassium Gluconate & Tripotassium Citrate (1:1) at 20%
 Potassium Bitartrate & Tripotassium Citrate (1:1) at 20%
 Potassium Gluconate, Potassium Bitartrate & Tripotassium Citrate (1:1:1) at 30%

25 The particles may be produced using standard spray drying equipment and typical conditions known to the art. Conditions may naturally vary depending on the nature of the equipment and the material being sprayed, but the person skilled in the art can readily determine the appropriate conditions in every case with only routine experimentation. Typical examples of conditions that produce dry powder with a moisture content of less than 5% and water activity in the desirable

30 range of from 0.05 to 0.30 at 25°C. Water activity (A_w) is the partial vapor pressure of water in a substance divided by the standard state partial vapor pressure of water. It is a measurement of the relative humidity of the sample in a closed chamber - basically A_w is the equilibrium humidity emitted by the sample material.

35 Typical parameters for use on a conventional tall-form tower spray dryer are:

Inlet temperature – 120-180°C

Outlet temperature – 70-95°C

The finished material size should be 20-200µm mean diameter by volume distribution, as measured by laser diffraction particle size instrument.

The disclosure is further described with reference to the following non-limiting examples.

5

Example 1: Preparation of test matrix

A test matrix was prepared by blending CapsulTM 1450, a sodium octenyl succinate-modified starch, and 25 DE maltodextrin in the weight proportion of 10:90. This is used as a control. When
10 salts were added, the proportion of maltodextrin is reduced by the proportion of salt added. The salts are shown in table 1.

Table 1 – Overview of salt samples

Sample No.	Salt/Level
1	Tripotassium Citrate 25%, Sugar 25%
2	Tripotassium Citrate 20%
3	Tripotassium Citrate 20% & Potassium Gluconate 10%
4	Magnesium Citrate 10%, Mannitol 20%
5	Magnesium Citrate 20% & Potassium Gluconate 10%
6	Potassium Gluconate 25%
7	Magnesium Gluconate 25%
8	Ferrous Gluconate 25%
9	Tripotassium Citrate 25%
10	Magnesium Citrate 25%
11	Calcium Citrate 25%
12	Calcium Magnesium Citrate 25%
13	Calcium Lactate 25%
14	Magnesium Lactate 25%
15	Calcium Fumarate 25%
16	Potassium Bitartrate 25%
17	Sodium Chloride 25%
18	Potassium Chloride 25%
19	Potassium Gluconate 10% & Tripotassium Citrate 10%
20	Potassium Gluconate 10% & Potassium Bitartrate 10%
21	Tripotassium Citrate 10% & Potassium Bitartrate 10%
22	Potassium Gluconate 10%, Tripotassium Citrate 10% & Potassium Bitartrate 10%
23	CONTROL SAMPLE (no salt)
24	Sodium Gluconate 25%

The loading in all cases was an addition to the matrix+salt of D-limonene at a rate of 15% of the matrix+salt.

The particles were prepared by blending the modified starch, maltodextrin and (where applicable) salt/salt mixture into warm water (40°C). To this, the D-limonene was added, and the mixture subjected to high shear mixing to emulsify the mixture to a mean particle size of less than 1.0 micron as measured by a laser diffraction particle size analyzer.

The emulsion was then spray-dried using an Anhydro PSD55 spray drying unit equipped with a rotary atomizer and a peristaltic delivery pump. Inlet and outlet temperatures were respectively 170°C (+5°C) and 95°C (+3°C). The powder was recovered by means of a cyclone separator.

Example 2: testing of oxidative stability

The various particles were tested for oxidative stability by determining the proportion of D-limonene remaining after various periods of storage. The samples were stored at 40°C and 30% relative humidity in LDPE bags of a type that did not provide a barrier to moisture absorption. Samples were analyzed by GC and MS. In addition to the control sample, there were also included two particles made using the same matrix and made using the same conditions and equipment, but with sugar in place of the salts, one with 50% sugar, the other with 40% sugar. These were designated S1 and S2, respectively.

The results are shown in Tables 2 and 3. Table 2 shows the proportion of D-limonene remaining and Table 3 shows the proportion of oxidation by-products present. An acceptable D-limonene loss was less than 10% of the original proportion (i.e. a limonene content of greater than 13.5%), or when the oxidation by-product proportion exceeded 2.5% of the original limonene proportion (at which level the sample fails organoleptically), no further measurements were taken.

Table 2 – Stability Study Results for sample D-Limonene assay values

Stability - Limonene Levels

Sample No.	Initial	4-Weeks	8-Weeks	12-Weeks	16-Weeks	18-Weeks	24-Weeks
1	14.18	13.51	12.83	11.99	11.40	-	-
2	15.69	14.67	13.78	12.74	11.87	-	-
3	13.91	13.73	13.53	13.26	13.08	-	12.92
4	14.44	14.33	14.22	14.10	13.96	-	13.94
5	14.59	14.52	14.41	14.26	14.18	-	14.33
6	14.75	14.46	14.27	13.86	-	-	-

7	14.58	14.19	13.88	13.60	-	-	-
8	14.79	14.09	13.89	13.25	-	-	-
9	14.66	14.37	13.88	13.82	-	-	-
10	13.45	12.64	11.96	11.34	-	-	-
11	14.04	12.99	12.23	11.61	-	-	-
12	13.78	12.66	11.85	11.28	-	-	-
13	14.64	13.29	12.59	12.04	-	-	-
14	14.11	13.40	12.84	12.50	-	-	-
15	16.76	15.91	15.21	14.67	-	-	-
16	14.82	14.22	13.50	13.04	-	-	-
17	14.52	14.20	13.79	13.35	-	12.87	12.54
18	14.82	14.44	13.98	13.55	-	13.16	12.86
19	14.67	14.41	14.31	14.10	-	13.98	13.92
20	14.68	14.46	14.10	13.87	-	13.13	13.01
21	14.91	14.62	14.48	14.20	-	14.16	14.03
22	14.85	14.60	14.55	14.01	-	13.82	13.70
23 (control)	14.38	13.67	13.25	12.71	-	-	-
24	14.57	14.26	14.18	14.09	-	-	-
S1	13.56	13.47	13.37	12.91	12.50	-	-
S2	14.12	13.39	13.24	12.71	-	-	-

Table 3

Stability - Oxidation Products Levels

Sample No.	Initial	4-Weeks	8-Weeks	12-Weeks	16-Weeks	18-Weeks	24-Weeks
1	0.31	1.23	2.23	3.40	4.03	-	-
2	0.41	1.58	2.37	3.41	4.09	-	-
3	0.39	0.77	1.02	1.41	1.69	-	2.60
4	0.67	0.60	0.80	0.67	0.88	-	2.48
5	0.50	0.51	0.60	0.51	0.69	-	1.18
6	0.47	0.62	0.83	0.83	-	-	-
7	0.68	1.04	1.55	1.29	-	-	-

6

8	0.65	0.98	1.38	0.97	-	-	-
9	0.40	0.56	0.73	0.55	-	-	-
10	0.48	1.15	2.62	3.05	-	-	-
11	0.76	2.09	2.94	3.23	-	-	-
12	0.55	1.99	2.97	3.09	-	-	-
13	0.60	1.93	3.55	4.03	-	-	-
14	0.57	1.19	2.32	2.36	-	-	-
15	0.66	1.51	2.67	2.88	-	-	-
16	0.35	1.03	1.61	1.77	-	-	-
17	0.29	0.57	1.06	2.04	-	2.26	3.25
18	0.29	0.52	0.95	1.86	-	2.16	3.17
19	0.31	0.58	0.82	1.21	-	1.22	1.89
20	0.25	0.62	0.91	1.51	-	2.62	3.80
21	0.26	0.64	0.81	1.30	-	1.33	2.14
22	0.27	0.51	0.65	1.38	-	1.50	2.37
23 (control)	0.51	1.90	2.54	-	-	-	-
24	0.45	0.72	0.74		-	-	-

From the tables, it can be seen that

- (i) the control and the two sugar-containing samples failed early.
- (ii) especially good results were obtained from samples 4, 5, 19, 21 and 22, that is:

5 Magnesium Citrate 10%, Mannitol 20%
 Magnesium Citrate 20% & Potassium Gluconate 10%
 Potassium Gluconate 10% & Tripotassium Citrate 10%
 Tripotassium Citrate 10% & Potassium Bitartrate 10%
 Potassium Gluconate 10%, Tripotassium Citrate 10% & Potassium Bitartrate 10%

10

Many of the other salts were acceptable for short duration storage times.

We claim:

1. A method of preparing spray-dried flavor-containing particles, comprising the addition of flavor to an aqueous, sugar-free matrix and spray-drying the resulting blend, the matrix comprising an emulsifier, a film former and at least one metal salt, selected from the ferrous, alkali metal and alkaline earth metal salts of citric, gluconic and tartaric acids.
2. A method according to claim 1, in which the salt is selected from potassium gluconate, tripotassium citrate, potassium bitartrate, sodium gluconate, magnesium gluconate and ferrous gluconate.
3. A method according to claim 1, in which the at least one salt is present at a concentration of from 10-30% by weight of the non-flavor particle constituents.
4. A method according to claim 3, in which the weight proportions of individual salts are selected as follows:

Potassium Gluconate	20-30%
Magnesium Gluconate	25%
Ferrous Gluconate	25%
Potassium Bitartrate	25%
Tripotassium Citrate	10-25%
Magnesium Citrate	20-30%
5. A method according to claim 1, in which more than one metal salt is used.
6. A method according to claim 5, in which the more than one salt is selected from one of the following combinations:
 - tripotassium citrate and potassium gluconate
 - tripotassium citrate and potassium bitartrate
 - potassium gluconate, tripotassium citrate and potassium bitartrate.
7. A method according to claim 6, in which the following weight proportions of salt are used:
 - Potassium Gluconate & Tripotassium Citrate (1:2) at 30%
 - Potassium Gluconate & Magnesium Citrate (1:2) at 30%
 - Potassium Gluconate & Tripotassium Citrate (1:1) at 20%
 - Potassium Bitartrate & Tripotassium Citrate (1:1) at 20%
 - Potassium Gluconate, Potassium Bitartrate & Tripotassium Citrate (1:1:1) at 30%.

8. A method according to claim 1, in which flavor is present at a proportion of up to 15% by weight of the particle.
- 5 9. A method according to claim 1, in which the matrix comprises from 10-90% by weight of the particle.
- 10 10. A spray-dried, flavor-containing particle comprising flavor in a sugar-free matrix, the matrix comprising an emulsifier, a film former and at least one metal salt, selected from the ferrous, alkali metal and alkaline earth metal salts of citric, gluconic and tartaric acids.
11. A spray-dried, flavor-containing particle according to claim 10, in which the flavor content is up to 15% by weight of the particle.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/061798

A. CLASSIFICATION OF SUBJECT MATTER
 INV. A23L27/00 A23L3/46
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 168 956 A1 (GEN FOODS CORP [US]) 22 January 1986 (1986-01-22) page 1, line 5 - line 17 page 5, line 10 - line 28; examples 1,3 -----	1-5,8-11
X	WO 03/045170 A1 (JENEIL BIOTECH INC [US]) 5 June 2003 (2003-06-05) page 8, line 27 - page 9, line 3; claims 7,9,12,15-19; examples 6-9 -----	1,2,10
X	US 2008/199592 A1 (FEXER WOLFGANG [DE] ET AL) 21 August 2008 (2008-08-21) paragraph [0087]; examples A-C ----- -/-	10,11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 July 2016

Date of mailing of the international search report

22/07/2016

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer

Kirchhoff, Eva

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/061798

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 064 856 A2 (GIVAUDAN SA [CH]) 3 January 2001 (2001-01-03) paragraph [0003] - paragraph [0004] paragraph [0017] - paragraph [0018] paragraph [0026]; examples 1,2 -----	1-11
A	US 5 720 978 A (MOREHOUSE ALPHA L [US]) 24 February 1998 (1998-02-24) column 1, line 45 - line 55; examples 3-5 -----	1-11
A	US 5 124 162 A (BOSKOVIC MARIJAN ANTE [US] ET AL) 23 June 1992 (1992-06-23) column 6, line 31 - column 7; claims 1-3,12-14 -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/061798

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0168956	A1	22-01-1986	CA 1226160 A 01-09-1987
		DE 3562441 D1 09-06-1988	
		EP 0168956 A1 22-01-1986	
		ES 8608815 A1 16-12-1986	
		IE 56539 B1 28-08-1991	
WO 03045170	A1	05-06-2003	AP 1764 A 08-08-2007
		AU 2002359517 A1 10-06-2003	
		BR 0214076 A 28-09-2004	
		CA 2465203 A1 05-06-2003	
		CN 1592584 A 09-03-2005	
		CR 7339 A 06-12-2004	
		CZ 20040635 A3 15-09-2004	
		EP 1455604 A1 15-09-2004	
		HU 0402523 A2 29-03-2005	
		IL 161631 A 30-11-2010	
		JP 2005510223 A 21-04-2005	
		KR 20040075863 A 30-08-2004	
		MX PA04004985 A 11-08-2004	
		OA 12728 A 28-06-2006	
		US 2002127325 A1 12-09-2002	
		US 2004126479 A1 01-07-2004	
		WO 03045170 A1 05-06-2003	
		ZA 200403474 A 14-07-2004	
US 2008199592	A1	21-08-2008	EP 1958520 A2 20-08-2008
			US 2008199592 A1 21-08-2008
EP 1064856	A2	03-01-2001	NONE
US 5720978	A	24-02-1998	CA 2034639 A1 30-11-1991
			US 5720978 A 24-02-1998
US 5124162	A	23-06-1992	AT 133538 T 15-02-1996
			AU 648208 B2 14-04-1994
			AU 2859392 A 27-05-1993
			BR 9204879 A 01-06-1993
			CA 2083444 A1 27-05-1993
			CN 1074933 A 04-08-1993
			DE 69208058 D1 14-03-1996
			DE 69208058 T2 22-08-1996
			EP 0545632 A1 09-06-1993
			ES 2084952 T3 16-05-1996
			HK 151996 A 16-08-1996
			JP H06220485 A 09-08-1994
			NZ 245237 A 25-11-1993
			US 5124162 A 23-06-1992