POTASSIUM ALUMINIUM SILICATE-BASED PEARLESCENT PIGMENTS, TYPES I, II AND III

Chemical and Technical Assessment (CTA)

Prepared by Daniel E. Folmer, Ph.D., and reviewed by Madduri V. Rao, Ph.D.

1. Summary

Potassium aluminium silicate-based pearlescent pigments (PAS-BPP) were first reviewed at the 74th Joint FAO/WHO Expert Committee on Food Additives (JECFA, 2011) for use as a colour in food. The specification for PAS-BPP prepared at the 74th JECFA encompassed all three types of pearlescent pigment identified by the sponsor: 1) Potassium aluminium silicate (PAS) coated with titanium dioxide only; 2) PAS coated with iron oxide only; and 3) PAS coated with both titanium dioxide and iron oxide. Tentative specifications were prepared at the 74th JECFA pending receipt of information including the following: the manufacture of all types of PAS-BPP, the stability of PAS-BPP, the particle size distribution for all available types of PAS-BPP and detailed information on sponsor-proposed analytical methods. This information was to be made available for the 77th JECFA (2013). While the sponsor did comment on all information requested by JECFA, not all information requested was received.

At the 42nd meeting of the Codex Committee on Food Additives (CCFA), the sponsor requested that JECFA evaluate PAS, also known as mica, as a carrier substrate for titanium dioxide and/or iron oxide. As indicated by information provided by the sponsor, PAS is not intended to be used in food itself as a food additive, but rather, will only be used as the compound pigment, known as PAS-BPP, when titanium dioxide and/or iron oxide have been formed as a coating on its surface through high temperature processes. As a result, all of the additive use data and the majority of toxicological data provided by the sponsor actually pertain to PAS-BPP, and not for PAS, the material initially requested for review by JECFA.

The approach taken by the sponsor to evaluate PAS as a carrier for titanium dioxide and/or iron oxide is consistent with the approach taken to regulate pearlescent pigments in the European Union (EU). The EU considers the pearlescent pigments to be mixtures of PAS and one or both of titanium dioxide and iron oxide. As such, the EU relies on the individual safety determinations and specifications for the separate entities of PAS, titanium dioxide and iron oxide. As indicated in DIRECTIVE 2003/114/EC, potassium aluminium silicate is permitted for use in the EU as a carrier for titanium dioxide and iron oxide, with specifications for the individual substances as provided in European Commission Regulation 231/2012 for PAS, titanium dioxide and iron oxide.

In the United States of America (USA), the compound pigment itself, under the name mica-based pearlescent pigments, is regulated under 21 Code of Federal Regulations (CFR) 73.350 rather than considering the components separately. As noted in 21 CFR 73.350, only titanium dioxide based pearlescent pigments are currently permitted in the USA. A reference is also made in 21 CFR 73.350 requiring that mica used to make the pearlescent pigments must conform to specifications for mica in 21 CFR 73.1496(a)(1).

Under the guiding principles that specifications are intended to apply to the additive as marketed and used in food, as well as represent the substance for which toxicological testing was performed, the 74th JECFA decided to prepare separate specifications for both PAS as well as PAS-BPP. Both sets of specifications prepared at the 74th JECFA were made tentative pending receipt of additional data.

The sponsor indicates that a total of 16 types of PAS-BPP are currently commercially available for use in food. The PAS-BPP are intended for use in a variety of candies, confectionaries, decorations, and in certain transparent alcoholic and non-alcoholic beverages. Use levels in candies,

confectionaries and decorations range from a low of 0.1% to a maximum of 1.25%, and for many products are only applied to the surface of the food. For beverages, the use levels are reported from a minimum of 0.02% to a maximum of 0.5%.

The 77th JECFA revised the tentative specifications for PAS-BPP made at the 74th JECFA in light of the additional information received by the sponsor. The combined tentative monograph for PAS-BPP prepared at the 74th JECFA was `split it into three monographs to cover all three types of PAS-BPP, as follows: 1) PAS-BPP, Type I represents PAS coated with titanium dioxide only; 2) PAS-BPP, Type II represents PAS coated with iron oxide only; and 3) PAS-BPP, Type III represents PAS coated with both titanium dioxide and iron oxide.

2. Description

PAS-BPP consist of platelets of potassium aluminium silicate (mica) to which titanium dioxide and/or iron oxide have been deposited by chemical reaction. The PAS-BPP exhibit a pearlescent color effect resulting from the partial transmittance and partial reflection of light as well as interference of light through the platelets. PAS-BPP can be produced with a variety of different pearlescent colour effects depending upon the initial PAS platelet particle size, the use of titanium dioxide or iron oxide alone or in combination, and the thickness of the coating of titanium dioxide and/or iron oxide on the PAS.

3. Method of Manufacture

PAS-BPP, Types I-III, are produced by reaction of PAS with soluble salts of titanium and/or iron followed by calcination at high temperatures. The resulting pigment consists of PAS coated with titanium dioxide and/or iron oxide. The pigments can be produced with a variety of different pearlescent colour effects depending upon particle size and the combination of titanium dioxide and iron oxide deposited on the potassium aluminium silicate.

4. Characterization

4.1 Composition

PAS-BPP consists of a coating of titanium dioxide (TiO2) and/or iron oxide (Fe2O3) on PAS. PAS is more commonly referred to as mica, or more specifically, muscovite mica, and has an idealized formula of KAl2[AlSi3O10](OH)2. PAS-BPP are differentiated into three types by JECFA as follows: 1) PAS-BPP, Type I represents PAS coated with titanium dioxide only; 2) PAS-BPP, Type II represents PAS coated with iron oxide only; and 3) PAS-BPP, Type III represents PAS coated with both titanium dioxide and iron oxide.

The sponsor has provided individual quality control specification monographs for 15 Candurin pigments. These consist of eight PAS-BPP, Type I pigments (Blue Shimmer, Gold Shimmer, Green Shimmer, Red Shimmer, Silver Fine, Silver Luster, Silver Sheen and Silver Sparkle); four PAS-BPP, Type II pigments (Brown Amber, Orange Amber, Red Amber and Red Luster); and three PAS-BPP, Type III pigments (Gold Sheen, Gold Luster, and Light Gold). Analytical data demonstrating adherence to specifications were provided for three of the pigments. Data on five batches each of Gold Shimmer (PAS-BPP, Type I), Orange Amber (PAS-BPP, Type II) and Gold Luster (PAS-BPP, Type III) were provided. In all cases, each batch of the pigments fell within required specifications as determined by the sponsor.

The sponsor indicated that there are four general particle size ranges for the PAS-BPP. These ranges are indicated, below, in Table 1.

Table 1. Range of particle sizes for PAS-BPP

	Range 1	Range 2	Range 3	Range 4
80% within range	5 – 25 µm	10 – 60 µm	10 – 150 µm	1 – 15 µm
d_{50} (median particle size)	7 – 14 µm	18 – 25 µm	65 – 82 µm	3 – 10 µm
Example: Candurin® Pi…	Gold Sheen	Gold Shimmer	Silver Sparkle	Silver Fine

Based on data contained in the quality control specifications for the 15 provided Candurin pigments, it can be confirmed that there are four general ranges for the "80% within range" specification, however, there appear to be as many as six ranges for the d50 (median particle size).

After deliberation during the 77th meeting, the Committee decided to add a statement in the Definition portion of the three PAS-BPP monographs indicating that pigment particles below a size of 100 nm shall not be present. The absence of particles below 100 nm seems consistent with the data provided by the sponsor. Information was also added to the Definition portion of each of the three PAS-BPP monographs indicating typical values for particle size, PAS content, and titanium dioxide and/or iron oxide content.

4.2 Impurities

The sponsor has recommended specifications for a number of potential metal impurities in PAS-BPP including arsenic, barium, cadmium, chromium, copper, mercury, nickel, lead, antimony and zinc. These metal specifications comprise the range of quality control metal specifications that the sponsor performs on PAS-BPP.

4.3 Stability

The sponsor indicates that they do not currently have analytical data pertaining to the stability of PAS-BPP under the typical preparation and storage conditions of specific foods. However, they indicate that, based on their longtime experience, they believe that PAS-BPP demonstrate excellent stability in general as well as when used in food products. In particular, they note that PAS-BPP are expected to have excellent thermal stability during food processing and storage, as the thermal conditions present during processing and storage are mild in comparison to the temperatures at which the PAS-BPP are made (calcined at 900°C). They also indicate that PAS-BPP are expected to have excellent chemical stability. In studies conducted with PAS-BPP in gastric and intestinal fluids, no indication was found that the fluids were able to extract the cations which were monitored during the study. Thus, the sponsor concludes that PAS-BPP should show excellent stability in foods, as the chemical conditions in foods are less aggressive than the chemical conditions in gastric and intestinal fluids.

In addition, the sponsor has provided the results of a 60 month warehouse-type stability study performed on three of the pigments (Silver Luster, Gold Sheen and Brown Amber). The sponsor analysed the amount of titanium dioxide or iron oxide in the pigments periodically over the course of the study. The study showed good agreement that the amount of titanium dioxide or iron oxide did not decrease over the course of the 60 months.

4.4 Rationale for Proposed Specifications

The proposed specifications were developed from information provided by the sponsor.

The sponsor has proposed specification limits for 10 metals (arsenic, barium, cadmium, chromium, copper, mercury, nickel, lead, antimony and zinc), some of which are typical in JECFA monographs (e.g., arsenic, lead and mercury), but others which are not typically seen in JECFA monographs. The sponsor was asked to comment on the need for the non-traditional metal specifications. They indicated that the 10 metals are those for which they routinely perform quality control. They indicated, however, that they believe sufficient quality control would be achieved with the inclusion of specifications for only mercury, lead, arsenic and cadmium.

The conditions proposed for the determination of the potential metal impurities is an extraction using 0.5 M hydrochloric acid rather than a complete digestion of the PAS-BPP. The sponsor notes that PAS-BPP particles will not be completely digested upon consumption, but rather only subject to extraction by stomach acids. They argue that boiling the PAS-BPP particles with 0.5M hydrochloric acid is more extreme than the conditions encountered in the body during digestion, and therefore is suitably conservative. They note that this method for heavy metal analysis is in line with the analysis requirement for E 171 (titanium dioxide) laid down in the Commission Regulation (EC) 231/2012 and the US FDA regulations 21 CFR 73.575

A specification for particle size was originally included in the tentative combined PAS-BPP monograph prepared at the 74th meeting of the Committee. Unfortunately, when taken as a Class (e.g., Type I, II or III), the range of particle sizes for the many commercially available pigments makes it difficult to establish a useful particle specification. As a result, the Committee decided to not include a particle size specification, but rather, to indicate in the Definition section of the monograph the typical particle sizes expected for the particular type of PAS-BPP.

A specification for pH was originally included in the tentative combined PAS-BPP monograph prepared at the 74th meeting of the Committee. Unfortunately, when taken as a Class (e.g., Type I, II or III), the pH range for the many commercially available pigments makes it difficult to establish a useful pH specification. As a result, the Committee decided to not include a pH specification in the monographs.

A specification for loss on drying (not more than 0.5%) was included in each of the monographs for PAS-BPP.

An assay was also established for percent titanium dioxide, percent iron oxide, and percent PAS, depending upon the type of PAS-BPP (e.g., Type III).

It was difficult to determine representative values for amounts of PAS, titanium dioxide and/or iron oxide in PAS-BPP. This was because, even for a particular type of PAS-BPP (e.g., Type III) each of the actual pigments is unique enough as to make generalizations of the specifications difficult. As a result, rather than include limits for the Assay, the phrase “As labelled” was used.

4.5 Analytical Methods

Some of the analytical methods proposed by the sponsor for PAS-BPP are comparable to tests included in the Combined Compendium of Food Additive Specifications for identity and purity (FAO JECFA Monographs 1, Volume 4, 2006). Other methods recommended by the sponsor are not typical JECFA methods, and may not have been used before in JECFA specification monographs. For example, the sponsor has recommended X-ray fluorescence (XRF) for the Assay for titanium dioxide and iron oxide, and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for determination of lead and seven other metals. The sponsor was asked if less expensive methods could be used (in line with JECFA’s preference to only include analytical methods that are accepted internationally but also are generally available in most international laboratories at a reasonable cost). Some methods, such as a titration method for determination of titanium and iron in the pigments, were provided. However, the Committee did not include these additional methods as they were felt to be less robust than the methods currently proposed in the monographs.

4.5.1 Loss on drying

Loss on drying is determined as recommended in Volume 4 of the FAO JECFA Monographs with the PAS-BPP sample heated at 105°C for 2 hours.

4.5.2 Assay for titanium dioxide, iron oxide and PAS

The sponsor has submitted information regarding the use of an XRF technique for the determination of titanium dioxide and iron oxide. They recommend the determination of PAS by difference from 100% (i.e., % PAS = 100% - % titanium dioxide + % iron oxide). However, JECFA believes that XRF is not commonly available in all international testing laboratories. As a result, the Committee recommends the use of ICP-AES using alkali fusion for sample preparation to determine the amount of titanium, iron and aluminium in the PAS-BPP sample. The percentage of titanium dioxide, iron oxide and PAS in the sample is then determined using the formulas for titanium dioxide, iron oxide and PAS, respectively.

4.5.3 Impurities soluble in 0.5 M hydrochloric acid

The sponsor provided individual specifications for barium, cadmium, chromium, copper, nickel, lead, antimony and zinc based on extraction with 0.5 M hydrochloric acid. Except for arsenic, the sponsor recommended analysis with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). JECFA believes that ICP-MS technique is not commonly available in laboratories. Therefore, a recommendation is made in the monograph to determine arsenic using an AAS (Hydride generation technique); antimony, barium, chromium, copper, nickel and zinc by ICP-AES technique; lead and cadmium using an AAS (Electrothermal atomization technique); and mercury using an AAS (Cold vapour generation) technique.

4.5.4 Identification tests for iron and titanium

Depending upon the type of PAS-BPP, an identification test was added for determining the presence of iron and titanium in the monographs. The tests are based on the ICP-AES assay method and use the analytical lines for Ti (334.941 nm) and Fe (259.940 nm).

5. Functional Uses

5.1 Food Categories and Use Levels

The sponsor has provided general food categories, use levels and examples of products to which PAS-BPP are added. The categories can broadly be described as confectionary, candy, decorations and beverages. Examples of the categories were provided, along with minimum effective use level, typical use levels, and maximum use levels. The examples and use levels are matched, below, in Table 2 as close as possible to food categories from the Codex General Standard for Food Additives (GSFA).

Table 2. Proposed food categories and use levels for PAS-BPP

GSFA Food Category	Examples	Minimum use level	Typical use level	Maximum Use level
5.1 Cocoa products and chocolate products including imitations and chocolate substitutes	Chocolate products coated with hard sugar[1]	0.1%	0.3-1.0%	1.25%
5.2 Confectionery including hard and soft candy, nougats, etc. other than food categories 05.1, 05.3 and	Licorice[1]	0.1%	0.2-1.0%	1.25%
	Jelly gums	0.1%	0.2-0.8%	1.25%

[1]Pigment is only applied to the surface of the product.

GSFA Food Category	Examples	Minimum use level	Typical use level	Maximum Use level
05.4	Marzipan[1]	0.1%	0.2-0.8%	1.25%
	Lollipops	0.1%	0.2-0.8%	1.25%
	Pastilles and lozenges[1]	0.1%	0.4-1.0%	1.25%
5.3 Chewing gum	Chewing gum[1]	0.1%	0.3-1.0%	1.25%
5.4 Decorations (e.g., for fine bakery wares), toppings (non-fruit) and sweet sauces	Hundreds and thousands, nonpareils[1]	0.2%	0.4-1.0%	1.25%
	Frosting	0.4%	0.6-1.0%	1.25%
14.1.4 Water-based flavoured drinks, including "sport," "energy," or "electrolyte" drinks and particulated drinks	Transparent water-based beverages, carbonated or non-carbonated	0.02%	0.08-0.3%	0.5%
14.2 Alcoholic beverages, including alcohol-free and low-alcoholic counterparts	Transparent alcoholic beverages, carbonated or non-carbonated	0.02%	0.08-0.3%	0.5%

6. Reactions and Fate in Foods

6.1 Determination of Levels in Food

As PAS-BPP are not soluble in water, the sponsor indicates that PAS-BPP can be analysed in beverages by filtering out the PAS-BPP, and then analysing the filtrate using the methods included in the specifications monograph. Similarly, the sponsor indicates that many solid foods to which the PAS-BPP are typically added are soluble in hot water (e.g. hard and soft candy). In these cases, the food sample can first be dissolved, filtered, and then the filtrate analysed based on the methods contained in the specifications monograph.

7. References

Ciullo, Peter A., editor. Industrial Minerals and Their Uses: a Handbook and Formulary. Noyes Publication, Westwood, New Jersey:1996, pp. 135-136.

Codex Alimentarius, 2010. Codex Alimentarius, Codex Committee for Food Additives (CCFA), CX/FA 10/42/15, January 2010, “Proposals for Additions and Changes to the Priority List of Food Additives Proposed for Evaluation by JECFA” pp. 7-10.

Codex Alimentarius, 2010. Codex Alimentarius, Codex Committee for Food Additives (CCFA), ALINORM 10/33/12, Report of the 42nd CCFA, Appendix XI, pp. 70-71.

European Commission, 1995. European Commission Directive 95/45/EC of 26 July 1995 laying down specific criteria concerning colours for use in foodstuffs.

European Commission, 2003. European Commission Directive 2003/114/EC of the European Parliament of the Council of 22 December 2003 amending Directive 95/2/EC on food additives other than colours and sweeteners. Official Journal of the European Communities, L24, p. 64.

European Commission, 2008. European Commission Directive 2008/84/EC of 27 August 2008, laying down specific purity criteria on food additives other than colours and sweeteners. Official Journal of the European Communities, L253.

European Commission, 2012. European Commission Regulation of 9 March 2012, laying down specifications for food additives listed in Annexes II and III to Regulation (EC) No. 1333/2008 of the European Parliament and of the Council.

FAO/WHO, 2010. CODEX STAN 192-1995 (Rev. 2010) General Standard for Food Additives, Annex B (Food Category System), pp. 9-47. Codex Alimentarius Commission, Joint Food Standards Program of the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO).

United States of America, 2006, Federal Register (FR), Volume 71, No. 106, June 2, 2006, pp. 31927-31929, Washington, DC, USA. Available at: http://frwebgate2.access.gpo.gov/cgi-bin/PDFgate.cgi?WAISdocID=yGuOqy/0/2/0&WAISaction=retrieve (accessed 30 May 2011).

United States of America, 2010, Code of Federal Regulations (CFR), Title 21: Food and Drugs (U.S. Food and Drug Administration), Section 73.350 (Mica-based Pearlescent Pigments). Washington, DC, USA. Available at: http://frwebgate.access.gpo.gov/cgi-bin/get-cfr.cgi (accessed 30 May 2011).

USFDA, 2005. United States Food and Drug Administration, March 1, 2005 Memorandum from H. Lee to P. DeLeo regarding CAP 8C0262, “Use of Pearlescent Pigments in Various Food Products – Update of Intake Estimates.”