Aluminium silicate (kaolin)

DOCUMENT M-CA, Section 6

RESIDUES IN OR ON TREATED PRODUCTS, FOOD AND FEED

Annex to EU Regulation 283/2013

Ownership Statement

The owner of this document and the data contained therein, unless otherwise stated, is Tessenderlo Group, N.V. This document or any part of it may not be disclosed to any third party without the authorization of Tessenderlo Group, N.V.

Registration authorities should not grant, amend or renew an authorization for other applicants based on the summaries of proprietary data and evaluation of information in this document unless they have received the agreement of Tessenderlo Group, N.V. or once the period of data protection has expired.

Version history[1]

Date	Data points containing amendments or additions and brief description	Document identifier and version number
28/02/2017	Initial applicant's dossier	MCA-S6_2018-02-28

[1] It is suggested that applicants adopt a similar approach to showing revisions and version history as outlined in SANCO/10180/2013 Chapter 4 How to revise an Assessment Report

Table of Contents

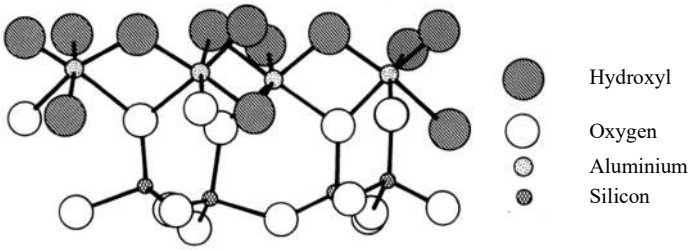
CA 6 RESIDUES IN OR ON TREATED PRODUCTS, FOOD AND FEED

Metabolism and residue studies were not considered relevant for evaluation nor necessary for the first inclusion due to the nature and properties of the active substance, aluminium silicate (aka kaolin), and the situation is unchanged for the renewal of approval.

Aluminium silicate (kaolin) is a clay that is essentially kaolinite; a hydrated aluminium silicate. The substance is ubiquitous within the environment and is naturally occurring within soil. Aluminium silicate is widely used within industry, where it is incorporated into paper, paints, rubbers, plastics, medicines, building materials and ceramic pottery.

The intake of aluminium silicate through its use as a plant protection product will be negligible based on the intended application. No MRLs (aluminium silicate is currently listed on Annex IV of Regulation 396/2005) or residue definitions have been allocated for aluminium silicate (kaolin), based on its use as a plant protection product. No MRLs or residue definitions are proposed as part of the renewal.

The (repeating) structure of hydrous kaolin is summarised as follows:



Kaolin is a layered silicate mineral, with one tetrahedral sheet of silica (SiO_4) linked through oxygen atoms to one octahedral sheet of alumina (AlO_6) octahedra. The structure is covalently bonded. Individual molecules of kaolin do not exist; it is a solid of infinite atomic structure and is consequently insoluble in water and all organic solvents.

Synonyms of aluminium silicate: aluminium silicate hydroxide, aluminium silicate hydroxide (kaolin), hydrated aluminium silicate, kaolin, kaolin (bound), oxo-oxoalumanyloxy-[oxo(oxoalumanyloxy)silyl]oxysilane;dihydrate.

It should be noted that while the active substance was ascribed the name ‘aluminium silicate’ during the original inclusion, the label is too broad to specify any one particular compound (it is analogous to naming ethanol as ‘alkyl alcohol’). The Notifier believes that kaolin is a better descriptor, as it distinguishes the active substance from other compounds which can be considered ‘aluminium silicates’. The bonding and structural properties of these other aluminium silicates can widely vary when compared to kaolin, which can lead to misunderstandings regarding the nature of the active substance compared to other compounds which are chemically classed as aluminium silicates (an instance of this is discussed further within section CA 6.2.2)

The metabolism and residues data are not deemed to be necessary to support the renewal of aluminium silicate (kaolin).

As a general note, to address the potential for residues within treated products, food and feed for the first inclusion of aluminium silicate (kaolin) under Directive 91/414, many of the provided cases referred to aluminium silicate being a commonly used food additive within the EU. Through Regulation (EU) No. 380/2012 (enforced from 1st February 2014) amending Annex II to Regulation (EC) No. 1333/2008, the use of a number of aluminium-containing food additives was restricted. Among these were calcium aluminium silicate, bentonite and aluminium silicate (kaolin), which are no longer permitted to be used as food additives within the EU. A transitionary period until 1st August 2014 was established by the regulation to allow manufacturers time to comply with the requirements, given the extensive use of aluminium compounds as coatings and colourants in existing produced food items.

As such, it is no longer considered appropriate to rely on such cases at renewal (which were based on kaolin being an approved food additive within the EU). It should however be noted that despite the food additive restriction, aluminium silicate (kaolin) is still considered to remain safe for the treatment of crops for human consumption based on the negligible exposure from the intended uses supported at renewal. Following the removal of aluminium silicate from the EU list of approved food additives, EFSA commented on the impact of the ruling on several aluminium-compound containing plant protection products (including aluminium silicate). The comments made at the '15th BfR Consumer Protection Forum'[1] indicate that where negligible exposure is demonstrated, the continued use of aluminium silicate as an insecticide on grape vines could be supported within the EU. Furthermore, the EFSA presentation noted that "*Aluminium silicate could be considered a candidate for the inclusion in Annex IV of Commission Regulation (EC) No 396/2005*".

Section 6.3 outlines the rationale supporting the case for negligible exposure to consumers, resulting from the treatment of grapevines with aluminium silicate (kaolin) at early plant growth stages (before the edible portion has formed).

[1] The presentation titled 'Activities of EFSA in the area of aluminium' was delivered by the EFSA representative, Prof. Dr George E.N. Kass (A member of EFSA's 'Food Ingredients and Packaging Unit'), on 26th November 2014 as part of the '15th BfR Consumer Protection Forum' titled "Aluminium in Everyday Life: A Health Risk? Intake of Aluminium from Food, Cosmetics and other Consumer Products". The presentation provides and overview and background covering the decisions leading to Regulation (EU) No. 380/2012. Slide 35 is the most pertinent to aluminium silicate.

The EFSA presentation is available to view directly from the BVL website:
http://www.bfr.bund.de/cm/343/activities-of-efsa-in-the-area-of-aluminium.pdf [accessed December 2017]

Details of the '15th BfR Consumer Protection Forum' are also available from the BVL website:
http://www.bfr.bund.de/en/event/15th_bfr_consumer_protection_forum__aluminium_in_everyday_life__a_health_risk__intake_of_aluminium_from_food__cosmetics_and_other_consumer_products_-191395.html [accessed December 2017]

CA 6.1 Storage stability of Residues

No residue data are required therefore storage stability is not relevant. Please refer to CA 6.3.

CA 6.2 Metabolism, Distribution and Expression of Residues

CA 6.2.1 Metabolism, distribution and expression of residues in plants

The DAR for aluminium silicate concluded the following:

"Kaolin is insoluble in water and therefore not taken-up and translocated by plants. It is also chemically inert and is not metabolised into other compounds. Any plant metabolism study is not required."

The same conclusion is considered to remain applicable for the renewal of aluminium silicate.

CA 6.2.2 Poultry

The DAR for aluminium silicate concluded the following:

"Kaolin is chemically inert, not bioavailable and not metabolised in mammals. Experience has shown that it is not absorbed through the gut wall. Any livestock metabolism study is therefore not required."

Despite the conclusion to revoke the use of aluminium silicate as a food additive within the EU, the above statement is still considered to remain valid. The revocation of food additive uses for aluminium compounds was primarily based on the conclusions of the EFSA report on the 'Safety of aluminium from dietary intake' (The EFSA Journal (2008) 754, 1-34). The report described a study which suggested that *"sodium aluminium silicate may be partly hydrolysed in the digestive tract, mainly in the abomasum (because of the low pH value) resulting in release of aluminium and silicate ions."* It should be clarified that the study was conducted on sodium aluminium silicate. Despite the similar name, the physical – chemical properties of sodium aluminium silicate (an ionically bound complex) are significantly different to those of aluminium silicate (which possesses strong covalent bonds). The differences between these compounds are discussed in greater depth in the vast literature available on clays and cay minerals[2], but briefly put, kaolin requires significantly harsh conditions (digestion is achieved using concentrated nitric acid at reflux, for periods of at least several hours)[3] or extreme temperatures / pressure in order to impact its structure. It is therefore not feasible from a chemical standpoint to consider that kaolin residues would dissociate to form aluminium ions within the comparatively less extreme conditions present

[2] For example, see Bergaya F. & G. Lagaly (Eds.), 2013, Handbook of Clay Science Second edition. Development in Clay Science 5. Elsevier, 1686pp (2 volumes).

[3] The degradation conditions for kaolin are described within the SW-846 EPA Test Method 3050B (1996), where the process was used to extract trace heavy metals from kaolin for analysis. The method was previously evaluated within the DAR for aluminium silicate (2008, RMS = Hungary), where it was concluded to be acceptable.

within the digestive tracts of livestock. Therefore, kaolin does not become bio-available when ingested.

Furthermore, aluminium silicate (kaolin) is ubiquitous within the environment. Prior to modern standards of hygiene and cleanliness, humans and livestock alike have been exposed for millennia to kaolin through contact within the environment (within water sources and on plants / harvested crops). Even in the present day, kaolin is likely to be frequently present on crops contaminated with soil or dust particles. Kaolin also remains widely used within pottery (including drinking vessels and crockery) which would present a direct route for consumers to ingest low levels of kaolin on a routine basis.

Despite the long history of human / animal exposure to kaolin, there are no scientific studies which kaolin is demonstrated to be toxic by ingestion. While the Commission's decision to revoke the use of aluminium silicate as a food additive may be viewed as over cautious, the lack of toxicological evidence to link kaolin exposure to increased aluminium ion concentrations in blood plasma and the known stability of kaolin by virtue of its physical / chemical properties, demonstrate that no risk will be posed to livestock (or humans by consumption of livestock products). The only route by which kaolin is considered to display toxicity is by chronic inhalation of aluminium silicate dust in occupational settings (resulting in a potential for pneumoconiosis); this aspect has been considered in greater detail in the M-CA S5 and M-CP S7 documents.

Relating to the representative uses supported at the renewal (grapevine), the OECD 'Guidance Document on Residues in Livestock' (Series on Pesticides No. 73) notes that grapes are not routinely fed to livestock within the EU (either as raw commodities or processed fractions). Consequently, it is not necessary to consider livestock dietary intakes as part of the renewal process. However, the Notifier requests that full consideration is made at the renewal of the

justification provided within this section, to permit the authorisation of additional crops in the future, which may be used within animal feed items.

CA 6.2.3 Lactating ruminants

No data are required for metabolism in animal. Please refer to point CA 6.2.2 for additional justification.

CA 6.2.4 Pigs

No data are required for metabolism in animal. Please refer to point CA 6.2.2 for additional justification.

CA 6.2.5 Fish

No data are required for metabolism in animal. Please refer to point CA 6.2.2 for additional justification.

CA 6.3 Magnitude of Residues Trials in Plants

CA 6.3.1 Grapevines

The D1 document outlines the GAP for grapevines.

Applications of the representative product, Surround WP, are made up to BBCH 65 *("Full flowering: 50% of flowerhoods fallen"*). The final application of Surround WP is made to grapevines before the formation of the edible part (grapes). Table 4 of the Commission's 'Guidelines on comparability, extrapolation, group tolerances and data requirements for setting MRLs' (SANCO 7525/VI/95 Rev. 10.3 – 13th June 2017) defines the term 'before forming of the edible part', and relates it to the current data requirements outlined within the current data requirements - Commission Regulation (EU) No 283/2013:

"The expressions 'after forming of the edible part' and 'before forming of the edible part' correspond to the definition given in the Annex to Commission Regulation (EU) No 283/2013 of 1 March 2013, Section 6.3. Magnitude of residue trials in plants):

> *For crops harvested after blossom (such as fruits or fruiting vegetables) a significant part of the consumable crop is present from full blossom (BBCH 65) onwards."*

Furthermore, kaolin is an inorganic mineral compound and it is not technically feasible for kaolin to be absorbed into foliar surfaces / translocate within plant systems (kaolin is insoluble in water and all organic solvents). Residues of kaolin therefore cannot accumulate on the surface of / within grapes, as a result of treatments made to grapevines prior to the formation of the fruit.

In addition, information is available to support this scenario within the published scientific literature. Spiers *et. al.* (2005) investigated the effects of kaolin clay application (using Surround WP)[4] on flower bud development, fruit quality, yield, and flower thrips populations, for blueberry

[4] *"Plants were established in 1988 in a Ruston fine sandy loam soil, and were planted according to a 3 x 3 Latin square. There were 6 replications, 2 treatments (kaolin and unsprayed), and 9 plants per experimental plot (total N = 108 plants). The*

plants. The results showed that for plants treated during the pre-fruit stage (~50% bloom, which equates approximately to BBCH 65) the kaolin residues were not significantly different from control plants in the amount of residue on the fruit (14.40% total solids[5] for the control samples and 14.58% total solids for the treated samples). The paper concluded (among other points) that *"When kaolin was applied before fruit set, yield was increased with no significant residue left on the fruit."*

Due to the similarities in the crop situation and the morphologies of grape berries and blueberries, it is considered that this information reliably supports the case that negligible residues are expected for on the harvestable fruit, based on treatments of grapevines (pre-fruit stage).

On the basis of the latest time of application (indicated within the GAP), the nature of the active substance and the literature information, the product will not yield residues within the raw agricultural commodity. As such, consumers will receive no / negligible exposure to kaolin on the as a result of consuming grapes from grapevines treated with Surround WP.

CA 6.4 Feeding Studies

CA 6.4.1 Poultry

No residue data are required in animals. Please refer to point CA 6.2.2.

CA 6.4.2 Ruminants

No residue data are required in animals. Please refer to point CA 6.2.2.

CA 6.4.3 Pigs

No residue data are required in animals. Please refer to point CA 6.2.2.

CA 6.4.4 Fish

No residue data are required in animals. Please refer to point CA 6.2.2.

application was a mixture of 1,077 g of kaolin (= 1,134 g Surround WP, Engelhard Corporation, Iselin, New Jersey) and 59 mL of a non-ionic surfactant (Silkin, Riverside/Terra Corp., Sioux City, Iowa) per 18.9 L (5 gal) of water. Therefore, each blueberry bush received about 20 g kaolin and control plants went unsprayed (0 g kaolin). Three applications were repeatedly made to the same plants during bloom (March 7, 2001), post-bloom (April 20), and pre-harvest (May 17). Liquid applications were applied with a pressurized 12 L backpack sprayer (SOLO™ Kleinmotoren GmbH, Sindelfingen, Germany). The plants were sprayed until drip and were visually inspected and re-sprayed to ensure complete coverage."

[5] The residue analysis method was described as follows:

"On each harvesting date, randomly selected berries were measured for chemical analysis, compression, and turbidity (residue). Thirty berries from each plant were swirled in 100 mL of distilled water for 1 min. to remove the residue from the berries. The water with residue was tested for turbidity using a Perkin-Elmer Lambda 3B UV/VIS spectrophotometer. Standards of 0, 10, and 100 mg · L^{-1} of kaolin clay (SurroundWP) were measured with the spectrophotometer prior to measuring the water with unknown amounts of residues. The standards were used to set up a linear regression and calculate the amount of kaolin clay residue left on the berries"

CA 6.5 Effects of Processing

CA 6.5.1 Nature of the residue

As a solid mineral, aluminium silicate (kaolin) is not readily degraded by typical household / industrial processes. It may only be structurally transformed by extreme temperatures / pressures (diagenesis or metamorphosis, which are two geological processes), or digested under harsh acidic conditions (concentrated nitric acid at reflux, for several hours). Consequently, kaolin will remain stable under the typical processing conditions described within OECD Guideline 507. A hydrolysis study is therefore not deemed to be necessary.

CA 6.5.2 Distribution of the residue in inedible peel and pulp

As noted under section CA 6.2.1:

"Kaolin is insoluble in water and therefore not taken-up and translocated by plants. It is also chemically inert and is not metabolised into other compounds."

CA 6.5.3 Magnitude of residues in processed commodities

No residue data are required therefore the magnitude of the residues in processed commodities is not relevant. Please refer to section CA 6.3.

CA 6.6 Residues in Rotational Crops

CA 6.6.1 Metabolism in rotational crops

Data to address this point is not required based on the intended representative use of Surround WP on grapevines. Kaolin is intended to be used on perennial (permanent / semi-permanent) crops, which according to the OECD 502 'Metabolism in Rotational Crops' guidance document, does not trigger the need for rotational crop metabolism to be provided. Similarly, limited field studies

are also not required for the same reason, according to the OECD 504 'Residues in Rotational Crops (Limited Field Studies)' guidance document.

CA 6.6.2 Magnitude of residues in rotational crops

No data are required to support the representative use (please refer to section CA 6.6.1).

CA 6.7 Proposed Residue Definitions and Maximum Residue Levels

CA 6.7.1 Proposed residue definitions

Residue definitions for aluminium silicate were not deemed to be necessary based on the conclusions of the original EU review (as stated within the aluminium silicate DAR (2008, RMS = Hungary) and within the EFSA conclusion (EFSA Journal 2012;10(2):2517)).

Tessenderlo Group, N.V. consider that this same decision regarding the residue definitions should remain unchanged for the renewal, and therefore cite the original justification which was accepted as part of the original EU review for aluminium silicate (kaolin):

- *Kaolin has no known mode of toxicity, is insoluble in water and does not become bioavailable when ingested.*
- *When applied to crops it leaves a white deposit on the surface that is easily removed by gentle rubbing and washing. This would be a normal procedure before marketing and/or consuming any foodstuff treated with kaolin.*
- *Kaolin is naturally present in the environment and is likely to be frequently present on crops contaminated with soil or dust particles.*
- *Kaolin does not degrade under environmental conditions.*
- *Kaolin cannot be analysed by conventional chromatographic techniques. Kaolin is a natural component of soil and therefore cannot be distinguished from existing clays, either in the soil or as an air born dust. It is impossible to differentiate between naturally present kaolin and kaolin from Surround® WP Crop Protectant.*

CA 6.7.2 Proposed maximum residue levels (MRLs) and justification of the acceptability of the levels proposed

The setting of MRLs for aluminium silicate (kaolin) associated with its use as a plant protection product is considered not necessary.

At the time of writing, aluminium silicate has already been provisionally[6] included on Annex IV of Commission Regulation (EC) No 396/2005 (as indicated within Commission Regulation (EC)

[6] Aluminium silicate (kaolin) is temporarily included in Annex IV, pending finalisation of EFSA's reasoned opinion in accordance with Article 12(1) of Commission Regulation (EC) No 396/2005. At the time of writing, the review of this substance by EFSA under this Article 12 process, has yet to be defined.

No 839/2008). It is considered that the MRL exempt status of aluminium silicate (kaolin) should remain, as a conclusion of the renewal assessment. According to the EU guidance document SANCO 2013-11188 rev.2, the substance fulfils three of the criteria required for MRL exemption:

Criterion 3 - The compound has no identified hazardous properties.

The properties of aluminium silicate are well understood and the compound is ubiquitous within the environment. While a number of notified classification have been submitted by companies to ECHA, all of these classifications relate to the toxicity of the compound when inhaled. A wealth of scientific literature is available concerning kaolin (refer to the results of the literature search) – none of the findings revealed any hazards related to the oral ingestion of kaolin.

Furthermore, neither an ADI nor ARfD value were considered to be necessary, based on the toxicological assessment (M-CA S5 and M-CP S7) and the requirements for 'Criterion 4' have been fulfilled.

Criterion 4 - Natural exposure is higher than the one linked to the use as PPP.

As noted within the discussion for Criterion 5, no consumer exposure is expected arising from the treatment of grapevines with Surround WP. Kaolin is ubiquitous within the environment and may be present within the consumer diet, following the consumption of commodities which are contaminated with soil / dust. Kaolin is also widely used within a diverse range of industries and is incorporated into paper, paints, rubbers, plastics, medicines, building materials and ceramic pottery. It is apparent that consumers are exposed to a wide range of sources of kaolin in daily life, which would far eclipse the negligible expose possible following the consumption of grapess treated at the intended GAP (refer to section 6.3).

Criterion 5 - No consumer exposure is forecasted linked to the mode of application of the PPP.

Applications of Surround WP are made prior to the formation of the edible commodity (refer to section 6.3), therefore consumer exposure arising from the intended GAP is not anticipated.

CA 6.7.3 Proposed maximum residue levels (MRLs) and justification of the acceptability of the levels proposed for imported products (import tolerance)

Please refer to point CA 6.7.2.

CA 6.8 Proposed Safety Intervals

The pre-harvest interval (PHI) for the proposed use of aluminium silicate on grapevines does not need to be specified. No supervised residues trials were submitted, nor would they be required to support a PHI, which is not considered to be a relevant parameter.

No re-entry period for livestock is required since the proposed use (grapevines) are not grazed by livestock. Nor is a withholding period required, as treated grapevines (or the resulting grapes) are not used as animal feeds within the EU (as indicated within the OECD 'Guidance Document on Residues in Livestock' - Series on Pesticides No. 73).

No re-entry period for man, or waiting period before handling treated produce, is required since there are no concerns for safety to workers exposed to residues remaining on the crop (refer to the M-CA S5 and M-CP S7 documents for further consideration of this point).

CA 6.9 Estimation of the Potential and Actual Exposure through Diet and other Sources

Acceptable Daily Intake (ADI) and Dietary Exposure Calculation

The toxicological information (M-CA S5 and M-CP S7) indicate that aluminum silicate possesses no chronic toxicity and therefore an acceptable daily intake (ADI) for this substance is not required. This same conclusion was reached during the original EU review (RMS = Hungary):

"As kaolin does not absorb into the organism through mucous membranes or the skin and an application for MRL exemption has been made, a proposal for ADI is not considered relevant."

Therefore, a quantitative chronic consumer risk assessment was not conducted and is not required.

Acute Reference Dose (ARfD) and Dietary Exposure Calculation

The toxicological information (summarised within M-CA S5 and M-CP S7) demonstrates that aluminium silicate is not acutely toxic and therefore an acute reference dose (ARfD) does not need to be allocated for this substance. This same conclusion was reached during the original EU review (RMS = Hungary):

"As kaolin does not absorb into the organism through mucous membranes or the skin and an application for MRL exemption has been made, a proposal for ARfD is not considered relevant."

Therefore, a quantitative acute consumer risk assessment was not conducted and is not required.

CA 6.10 Other Studies

No additional studies are necessary to support the renewal of aluminium silicate.

CA 6.10.1 Effect on the residue level in pollen and bee products

No data required for residue level in pollen and bee products. Please refer to point CA 6.

REFERENCES

Section	Authors	Year	Title	Reference
MCA 6 (point CA 6.3.1.)	Spiers *et. al.*	2005	Effects of Kaolin Clay Application on Flower Bud Development, Fruit Quality and Yield, and Flower Thrips [*Frankliniella spp. (Thysanoptera: Thripidae)]* Populations of Blueberry Plants.	Small fruits review, pages 73-84