Report of the Scientific Committee of the Spanish Food Agency for Food Safety and Nutrition (AESAN) in relation to the use of calcium carbonate as a processing aid in the process for obtaining virgin olive oil

Scientific Committee members

Rosaura Farré Rovira, Francisco Martín Bermudo, Ana María Cameán Fernández, Alberto Cepeda Sáez, Mariano Domingo Álvarez, Antonio Herrera Marteache, Félix Lorente Toledano, Mª Rosario Martín de Santos, Emilio Martínez de Victoria Muñoz, Mª Rosa Martínez Larrañaga, Antonio Martínez López, Cristina Nerín de la Puerta, Teresa Ortega Hernández-Agero, Perfecto Paseiro Losada, Catalina Picó Segura, Rosa María Pintó Solé, Antonio Pla Martínez, Daniel Ramón Vidal, Jordi Salas-Salvadó, Mª Carmen Vidal Carou

Secretary

Vicente Calderón Pascual

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Working Group

Rosaura Farré Rovira and
Mª Rosa Martínez Larrañaga (Coordinators)
Ricardo López Rodríguez (AESAN)

Abstract

Calcium carbonate ($CaCO_3$) has been authorised as a food additive (E 170) with the functional category of anti-caking/free flow agent agent, surface colouring and stabiliser.

An evaluation on the use of calcium carbonate as a processing aid in the process of obtaining virgin olive oil has been requested.

Calcium carbonate is a substance that is authorised in human foodstuffs but its acceptable daily intake has not been established and its use does not lead to technically avoidable residues.

Once the application dossier of the calcium carbonate (Microliva) as a processing aid in the process of obtaining virgin olive oil has been evaluated and from the information provided by the applicant and in the doses and conditions proposed, the Scientific Committee concludes that the use of the calcium carbonate as a processing aid in this process is safe.

Key words

Calcium carbonate, Microliva, E 170, processing aid, olive oil.

Introduction

The company Minera del Santo Ángel S.L., with registered office in Gilena (Seville), has requested authorisation to use the product Microliva, micronized limestone the main constituent of which is calcium carbonate ($CaCO_3$), with a content of more than 98% and a heavy metal content less than that established by the European Regulation for the food additive E 170 (calcium carbonate). The Company proposes the product Microliva, as a processing aid in the process for obtaining virgin olive oil.

Therefore, the Executive Director of the Spanish Agency for Food Safety and Nutrition (AESAN) has asked the Scientific Committee to assess the safety of using calcium carbonate (Microliva) as a processing aid.

To perform this assessment, the Scientific Committee has considered the "Guidelines indicating the necessary documentation for the assessment of processing aids intended for use in human food" (AESAN, 2010). These guidelines are applicable to processing aids that may be used in the manufacture of products intended for human consumption, excluding enzymes, biocides and solvents from the field of application.

Calcium carbonate ($CaCO_3$) E 170, an additive analogue to the product Microliva, is authorised as a food additive, functional category: anti-caking/free flow agent (Royal Decree 142/2002 dated 1 February 2002, from the Ministry of Health and Consumer Affairs, approving the positive list of additives other than colorants and sweeteners for use in the preparation of food products, and their conditions of use) (Real Decreto, 2002), and the JECFA (Joint FAO/WHO Expert Committee on Food Additives) have established an unspecified Acceptable Daily Intake (ADI) (JECFA, 1965). Therefore, in accordance with the criteria established in the above-mentioned guidelines, the calcium carbonate (Microliva) is classified in situation 1: substance authorised in human food whose use is authorised *quantum satis* (no maximum level specified). In line with this situation, the applicant for the product Microliva presents information relating to the following aspects:

- Administrative data and general introduction.
- Physical and chemical characteristics.
- Technological function.

Administrative data and general introduction

1. Exact designation and commercial name

The product with the commercial name, Microliva, proposed as a processing aid, is micronized limestone composed of calcium carbonate with a content of more than 98%.

2. Intended use of the substance

Processing aid in the process for obtaining virgin olive oil.

3. Authorised uses in human food

Calcium carbonate ($CaCO_3$) is authorised as a food additive (E 170) with the functional category: anti-caking/free flow agent, surface colorant and stabiliser and is synonymous with limestone.

The standards for the identity and purity of calcium carbonate (E 170) are established in the Annexe to Royal Decree 2107/1996, dated 20 September 1996, which establishes the standards for the

identity and purity of colorants used in food products (Real Decreto, 1996), and subsequently in Royal Decree 1465/2009 (Real Decreto, 2009).

4. Acceptable Daily Intake

ADI: not specified (*quantum satis* use*)* (JECFA, 1965).

Physical and chemical characteristics

1. Composition and detailed formulation

The applicant states that the product Microliva is micronized limestone composed of calcium carbonate ($CaCO_3$) with a content of more than 98%.

Table 1 lists the composition and physical and chemical characteristics of the calcium carbonate (Microliva) and the requirements to which the calcium carbonate must comply (E 170) for use as a food additive.

Table 1. Declared composition of the calcium carbonate (Microliva) and calcium carbonate (E 170)

Calcium Carbonate (Microliva)	Calcium Carbonate (E 170)[a]
–Microliva, is micronized limestone composed of very pure calcium carbonate ($CaCO_3$), with a content of more than 98% –CAS No: 471-34-1 –Molecular weight: 100.09 g/mol –Practically insoluble in water (solubility: 0.0014 g/100 ml) and –Totally insoluble in non polar solvents such as olive oil	–Limestone: $CaCO_3$[a] –Molecular weight: 100.1 g/mol –Content not less than 98% of anhydrous material –White, crystalline or amorphous, odourless and tasteless powder –Solubility: practically insoluble in water and in alcohol. Effervescent dissolution in diluted acetic acid, in diluted hydrochloric acid and in diluted nitric acid, and the solutions obtained, after boiling, give positive results in the calcium detection tests

[a]Royal Decree 2107/1996 and 1465/2009.

2. Product specifications

The applicant has submitted the following information concerning the composition of the product Microliva (Table 2). Table 2 also includes all the specifications (purity criteria and limits) for the authorised additive, calcium carbonate or limestone E 170 and for the product Microliva, for comparison with respect to the calcium carbonate.

Table 2. Criteria required for the additive E 170 (Royal Decree 1465/2009) and tests submitted by the applicant for the proposed processing aid

Specifications for calcium carbonate (E 170)		Specifications Microliva		Calcium Carbonate (Microliva)
Content not less than 98% of anhydrous material		≥98.0%		98.6%
Loss on drying: not more than 2% (200 ºC, 4 hours)		≤2%		0.18%
Substances insoluble in acids: not more than 0.2%		≤0.2%		0.12%
				0.18%
Alkaline and magnesium salts: not more than 1.5%		<1%		<0.25%
Fluoride: not more than 50 mg/kg		<50 mg/kg		<2 mg/kg
Sb	<100 mg/kg individually or together	<100 mg/kg individually or together	Sb	not detected (<0.01 mg/kg)
				<2 mg/kg
				<0.1 mg/kg
Cu			Cu	1.11 ± 0.04 (n=3)
				5.1 mg/kg
				<1 mg/kg
Cr			Cr	12.94 ± 0.11 (n=3)
				<2 mg/kg
				5.78 mg/kg
Zn			Zn	1.61 ± 0.07 (n=3)
				19.7 mg/kg
				<1 mg/kg
Ba			Ba	19.71 ± 0.24 (n=3)
				39.4 mg/kg
				4.19 mg/kg
Arsenic: not more than 3 mg/kg		<3 mg/kg		0.051 ± 0.003 (n=3)
				<2 mg/kg
				0.1 mg/kg
Lead: not more than 10 mg/kg		<3 mg/kg		0.238 ± 0.021 (n=3)
				<2 mg/kg
				<0.05 mg/kg
Cadmium: not more than 1 mg/kg		<1 mg/kg		0.143 ± 0.004 (n=3)
				<0.5 mg/kg
				<0.01 mg/kg
–		Fe_2O_3: <0.02%		0.01%
–		pH 8.5-10.5		8.8
–		Residue after 44 micron sieving: <0.1%		0.0%

The metal analysis was performed by the Central Service for Research Support (SCAI) at the University of Cordoba, using graphite furnace and hydride generation atomic absorption spectrophotometry.

At the request of the Scientific Committee, the applicant submitted additional test results with respect to the purity criteria and limits.

3. Procedure for obtaining the calcium carbonate

Microliva is obtained by subjecting the natural limestone (sedimentary rock mainly composed of calcite ($CaCO_3$)) to a physical process consisting in the extraction, milling and micronization using mechanical methods only (hammer and ball mills, and dynamic selection of particle size using air selectors), without using any additives or chemical or biochemical treatments. The product is presented in white powder form, and packed in a paper carton suitable for use in the food industry.

Technological function

As indicated by the applicant, the micronized calcium carbonate must be added to the thermobeater at the start of the beating of the oil released during the crushing or milling process to ensure it is evenly distributed. Moreover, the addition of the dose to the mill should be performed automatically; manual addition is not recommended.

For the Department of Chemical, Environmental and Material Engineering at the University of Jaen, the mechanism of action of the calcium carbonate is purely physical, and can be explained by the action of *Van der Waals* forces, absorbing the micro-drops of oil retained on the walls of the cells, leading to the formation of drops and therefore increasing the quantity of oil released. With respect to the calcium carbonate residue remaining in the oil, given its high specific weight (2.72 g/cm^3), the calcium carbonate is easily eliminated during the centrifugal process together with the solid waste or pomace.

1. Level of use requested

According to the applicant, based on the performance studies carried out, the calcium carbonate dose to be used is between 1% and 2% of the weight of the crushed olives, depending on the variety of olive, the humidity and the olive maturity index.

The efficiency studies, discussed below, in which the extraction yield is assessed according to the variety of olive, have been carried out with doses of 1% and 2%.

In addition, in a nonlinear regression analysis the optimum dose is described for the *Picual* olive as 3.1% and for the *Arbequina* olive as 2.1%. In this test it is observed that after 2% and for a broad treatment level rango, the variation in the extraction yield is small.

2. Justification for use, interest and efficiency

The purpose of using the product Microliva during the extraction of the oil is to recover the majority of the oil retained by the pastes, also helping to correct the cellular structure and to modify the physical and chemical properties of these pastes. Therefore, the pulverised calcium carbonate has a high lipophilic nature able to retain up to 26 g of oil per 100 g of carbonate through a physical

mechanism of action. This mechanism permits the absorption of the micro-drops of oil retained on the cell walls, thus increasing the quantity of free oil.

In this respect, the results were submitted of the laboratory tests carried out by the University of Jaen on olive samples of the *Picual, Hojiblanca* and *Arbequina* varieties to which calcium carbonate was added at 1% and 2%. The results obtained indicate that the calcium carbonate improves the extraction yield by 1.37 and 0.98 points (kg oil/100 kg olive) for the *Picual* variety, 3.73 points for the *Hojiblanca* variety and 2.56 points for the *Arbequina* variety.

In addition, a comparative study was made of the extraction efficiency of the calcium carbonate and talc at doses of 1% and 2% in *Picual* and *Arbequina* varieties. Based on the results obtained, no statistically significant differences were observed between the use of the carbonate and of the talc.

The Scientific Committee considered that on adding micronized calcium carbonate to the crushed olive paste, in which there is an aqueous medium resulting from the plant water in the fruit, which normally has an acid pH of between 4.5 and 5.2, the calcium carbonate may be soluble in this medium. In these conditions, its chemical activity may be demonstrated due to the presence of bicarbonate-carbonate which, although in low concentrations, may be inconsistent with the concept of chemical inactivity, established in Regulation (EC) No 1513/2001 (EU, 2001), in order to consider that it functions as processing aid in obtaining virgin olive oil. Therefore, the Company was asked to perform studies on the olive paste with the addition of calcium carbonate that demonstrated its behaviour and permitted the demonstration of chemical inactivity or activity.

With respect to chemical inactivity, the applicant submitted a report on the study carried out by the experimental oil mill at the Instituto de la Grasa (CSIC), Seville. This study consisted in the performance of a test on an industrial scale in order to compare the efficiency of calcium carbonate, against a control, in the processing of virgin olive oil from olives of the *Hojiblanca* variety. The quantity of calcium carbonate added at the beginning of the beating stage was 2%.

The study indicates that almost no differences were observed in the chromatic parameters or from a sensorial point of view. In addition, the analytical results show that there are no significant differences between the control oil and the oil obtained with the calcium carbonate with respect to the composition of methyl esters, sterols, erythrodiol, uvaol and total sterols (Table 3).

Table 3. Composition in sterols (%) and methyl esters of the fatty acids and content of erythrodiol, uvaol (%) and total sterols (mg/kg)

Sterolic composition (%)	Control	Microliva (dose 2%)	Methyl esters (%)	Control	Microliva (dose 2%)
Cholesterol	0.2	0.1	Myristic	0.02	0.0
Brasicasterol	0.0	0.0	Palmitic	8.1	8.2
24-methylene cholesterol	0.1	0.1	Palmitoleic	0.6	0.6
Campesterol	3.0	3.0	Margaric	0.2	0.2
Stigmasterol	0.4	0.4	Margaroleic	0.3	0.3
Delta-7-campesterol	0.0	0.0	Stearic	4.1	4.0
Clerosterol	1.0	1.0	Oleic	78.2	78.2
Beta sitosterol	86.3	86.7	Linoleic	6.7	6.7
Sitostanol	0.5	0.5	Linolenic	0.8	0.8
Delta-5-avenasterol	6.9	6.7	Arachic	0.5	0.5
Delta-5,24-stigmastadienol	0.6	0.5	Eicosenoic	0.3	0.3
Delta-7-stigmastadienol	0.3	0.3	Behenic	0.1	0.1
Delta-7-avenasterol	0.6	0.6	Lignoceric	0.1	0.1
Apparent Beta sitosterol	95.3	95.4			
Erythrodiol + Uvaol	2.4	2.6			
Total sterols (mg/kg)	1,500	1,500			

With respect to the changes in the pH that may be caused by the addition of calcium carbonate, laboratory tests have been carried out using olives of the *Picual* and *Hojiblanca* varieties. The results of these tests reveal a slight increase in pH in the aqueous phase of 0.4 and 0.5 units, respectively. With respect to the acidity of the oil after vertical centrifuging, this is 0.17% in the control and 0.15% in the sample with calcium carbonate.

The report submitted concludes that, in accordance with certain comparative tests performed on the oils, practically no differences are observed with respect to the purity, quality and composition of the oils.

In addition, with respect to the efficiency of the treatment, the results obtained indicate that treatment with calcium carbonate at 2% resulted in an increase of 15.37% in the oil yield, compared to the control sample. Moreover the oil obtained was cleaner on leaving the decanter and the percentage of humidity and solids was reduced by approximately 50%. In addition, in the vertically centrifuged oils differences were only observed in the impurity content, which was lower in the oil treated with calcium carbonate as this enhances their separation.

Based on the information provided, the chemical inactivity of the calcium carbonate is considered to be demonstrated.

Nevertheless, queries have been raised concerning the situation produced due to the permanence of the calcium carbonate in the pomace, especially with respect to the processes involved in its industrial exploitation: drying, extraction and subsequent refining. In this respect, the applicant has submitted a report drafted by the Department of Chemical, Environmental and Material Engineering

at the University of Jaen which indicates that the industrial exploitation of the pomace resulting from the obtaining of virgin olive oils is essentially one process in two stages: drying of the humid pomace and extraction with solvents in order to obtain crude olive pomace oil. The presence of calcium carbonate should not cause any problems during the pomace drying stage, as its thermal decomposition only occurs at temperatures of above 840 ºC and produces CO_2 and CaO, neither of which are toxic or result in toxic products. At the operating temperatures of the pomace oil extraction plant, the calcium carbonate behaves as an inert material which in no way interferes with any of the stages of the process.

When the pomace is dry, the pomace oil is extracted using hexane, a non-polar solvent in which the calcium carbonate is totally insoluble, and therefore it should not be present in the extracted oil.

In addition, these pomaces are maintained in open air tanks for periods of up to six months. The presence, in very limited quantities, of a processing aid such as calcium carbonate, which is basic, may neutralise part of the acidity generated in the tank and some of the free fatty acids. This is a benefit with respect to the refining process, as the lower the level of acidity of the oils, the less effort is required to neutralise them at the refinery.

Conclusions of the Scientific Committee

The Scientific Committee, having assessed the application to use calcium carbonate (Microliva) as a processing aid in the procedure for obtaining virgin olive oil, concludes that, based on the information provided by the applicant and on the doses and conditions proposed, the use of calcium carbonate as a processing aid in the procedure for obtaining virgin olive oil is safe.

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