MAGNESIUM DIHYDROGEN DIPHOSPHATE

Chemical and Technical Assessment

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1. Summary

At its 76th Meeting, the Committee was asked to evaluate the safety of Magnesium Dihydrogen Diphosphate (MDHDP) for use as acidifier, stabilizer and raising agent. This Chemical and Technical Assessment summarizes data and information on MDHDP submitted by Chemische Fabrik Budenheim KG[1], in a dossier dated December, 2011.

MDHDP is intended for use as an alternative to currently permitted sodium-based raising agents and acidifiers, primarily used for baking purposes. MDHDP is the acidic magnesium salt of the diphosphoric acid and is chemically very similar to already evaluated calcium dihydrogen diphosphate and mono-magnesium phosphate. MDHDP is the acidic magnesium salt of diphosphoric acid. It is manufactured by adding an aqueous dispersion of magnesium hydroxide slowly to phosphoric acid, until a molar ratio of about 1:2 between Mg and P is reached. The temperature is held under 60^o during the reaction. At the completion of the reaction, about 0.1% hydrogen peroxide is added and the slurry is then dried and milled.

MDHDP is a white powder, slightly soluble in water. MDHDP is designed to be used as an acidifier and raising agent, primarily in self raising flour, noodles (oriental style), bread & rolls, batters, processed cereals and fine bakery wares. Typical use levels range from 0.5 – 6.5 g (as P)/kg.

2. Description

MDHDP (chemical formula: $MgH_2P_2O_7$) is the acidic magnesium salt of the diphosphoric acid. Its INS number is 450 (ix) and the CAS number is 20768-12-1. MDHDP is a white crystalline or fine powder. It is slightly soluble in water (ca. 1.0 g per liter). The chemical properties of MDHDP are similar to calcium dihydrogen diphosphate [INS 450 (vii)] and monomagnesium phosphate [INS 343(i)]. It is designed for use as an acidifier, stabilizer and raising agent for baking purposes; and as an alternative to the sodium-based acidifiers and raising agents.

MDHDP has not been evaluated previously by the Committee. However, several other mono and di and polyphosphates were evaluated by the Committee. Phosphates were evaluated as a group of additives. A maximum tolerable daily intake (MTDI) of 70 mg/kg BW (expressed as phosphorous), from all food sources, was established at the 26th JECFA (1982)[2].

3. Method of Manufacture

MDHDP is the acidic magnesium salt of diphosphoric acid. It is manufactured by adding an aqueous dispersion of magnesium hydroxide slowly to phosphoric acid, until a molar ratio of about 1:2

between magnesium and phosphorous is reached. The temperature is held under 60^o during the reaction. About 0.1% hydrogen peroxide is then added to the reaction mixture to oxidize all ingredients. The slurry is then dried in a drum dryer (180 - 220^o) or by using any other suitable drying technique, to evaporate water and residual hydrogen peroxide, until a loss on ignition reaches <12%. The resulting granules are then milled into a fine powder and packed.

Step 1: $Mg(OH)_2 + 2\ H_3PO_4 \rightarrow Mg(H_2PO_4)_2 + 2\ H_2O$
Step 2: $Mg(H_2PO_4)_2 \rightarrow MgH_2P_2O_7 \downarrow + H_2O \uparrow$

Other salts such as sodium, potassium or calcium are intentionally added, at low levels to adjust desired baking properties. In addition, natural calcium which may occur, depending on the source of magnesium in the magnesium hydroxide. These ions influence the properties such as solubility rate.

4. Characterization

4.1 Composition

The composition of MDHDP was provided by the sponsor. In one study the composition was determined using the product obtained in three production trials. The average data obtained from the three production trails is given in Table 1:

Table 1: Average Composition of MDHDP

Analyte	Range (%)	Mean	Std. Dev.
Phosphorus pentoxide	68.4 – 70.1	69.5	0.52
Magnesium oxide	18.6 – 19.1	18.9	0.33
Sodium oxide	0.20 – 1.35	0.46	0.33
Loss on Ignition	10.7 – 11.4	11.1	0.32

4.2 Possible impurities (including degradation products)

Raw materials used in the production of MDHDP are similar to those being used in the production of magnesium phosphate, magnesium hydrogen phosphate or trimagnesium phosphate. The quality of raw materials is controlled by well defined specifications based on the JECFA specifications as well as Food Chemicals Codex[3]. Impurities such as orthophosphate, fluoride and toxic elements (lead, cadmium, arsenic and aluminium) in the final product might come from the raw materials or as a consequence of the manufacturing process. Diphosphate salts usually contain some quantities of ortho-, tri- and polyphosphates. Controlling the reaction conditions, use of oxidants and following good manufacturing practices allow to keep them to the lowest level as possible. Table 2 provides representative data on the levels of impurities present in MDHDP.

Table 2: Levels of impurities in MDHDP

Impurity	Trial 1(mg/kg)	Trial 2(mg/kg)	Trial 3(mg/kg)	Trial 4(mg/kg)
Fluoride	2	<1	2	2
Lead	<1	<1	<1	<1
Arsenic	<1	<1	<1	<1
Cadmium	<1	<1	<1	<1
Mercury	<1	<1	<1	<1
Antimony	<5	<5	<5	<5
Potassium	9	34	11	27
Sulphate	320	335	370	290
Chloride	<20	<20	<20	<20
pH (1% soln)	2.9	3.3	2.7	3.1
Orthophosphate (as P_2O_5, %)	3.8	4.7	3.8	4.1
Tri-polyphosphate (as P_2O_5, %)	0.1	<0.1	0.1	0.1

4.3 Rationale for proposed specifications

Calcium content in MDHDP must be restricted as there is a risk that calcium hydroxide instead of magnesium hydroxide may be used in its manufacture. Calcium is restricted by not more than 0.4% to restrict the use of any impure magnesium hydroxide in the manufacturing process of MDHDP.

Sodium and potassium can occur in MDHDP due to two reasons: a) intentionally added in order to adjust the crystalline structure of the product for a better baking performance, or b) they occur naturally in the raw materials.

The availability of sufficiently pure raw materials makes it is possible to manufacture MDHDP with arsenic, lead and cadmium levels lower than 1 mg/kg. The mercury levels in MDHDP reported in the dossier submitted by the sponsor are below 1 mg/kg. A maximum limit for mercury was considered not necessary as none of the raw materials or the manufacturing process contribute to mercury contamination.

Aluminium salts are a naturally occurring contaminant in magnesium salts. It varies in composition based on the geographical regions from where the magnesium salts are mined. However, availability of magnesium salts with low aluminium salt content as well as further purification bring aluminium levels of below 50 mg/kg in MDHDP. Aluminium salts may also be intentionally added (at levels of more than 500 mg/kg) to improve the raising properties by retarding the carbon dioxide release. A maximum level of 50 mg/kg has been set in the specifications to control the quality of raw materials used in the manufacture of MDHDP as well as avoid intentional addition of aluminium salts.

A microbiological contamination is unlikely due to the conditions used in the production process of MDHDP (drying temperatures above 200°C). All raw materials used are inorganic and synthetic in nature. The product is has a pH-value of less than 1 and does not warrant setting any microbiological specifications.

According to the sponsor, MDHDP has a loss on ignition >12%, and consequently does not have sufficient storage stability to establish a limit on loss of ignition. Excess water in the product leads to lumping as well as accelerated hydrolysis of diphosphates to orthophosphates with simultaneous acidification. The product with loss on ignition <12%, is stable for about 2 years, when stored at or below 25°C and 60 % RH. However, shelf-life can differ, especially under high temperature and humidity conditions, leading to formation of lumps as well as its degradation to orthophosphate, induced by auto hydrolysis.

The particle size of MDHDP has an influence on its reaction rate in the products where its addition is for a specific technological purpose. The finer the particle size of the material, the quicker it reacts due to the larger surface area. To produce a more retarded (gradually soluble) product, it is necessary to control the particle size distribution of MDHDP which fits two aims: (a) not being too fine or too coarse to facilitate its homogenic distribution in dry blends and (b) to obtain a product preferably as coarse as possible to achieve better retardation. However, it is required to avoid spot discolouration in the food product from a too slow reacting material. The average particle size of MDHDP produced in three production trials ranged between 16.7µm and 42.4µm.

4.4 Analytical methods

Most of the test methods included in the specifications monograph of MDHDP are standard methods, published in the Combined Compendium of Food Additive Specifications FAO JECFA Monographs, Vol.1(4), 2006[4]. The sponsor has submitted data in different production trials of MDHDP following the analytical methods outlined below. However, most methods used by the sponsor are validated and are capable of providing sufficiently accurate and reliable data.

4.4.1 Determination of phosphorous, magnesium and calcium

The sponsor has submitted data on P_2O_5, CaO and MgO in MDHDP using x-ray fluorescence (XRF) technique. However, XRF is not commonly available in testing laboratories and also requires an expensive platinum/gold crucible. The Committee recommends the use of most commonly available instrument 'Inductively Coupled Plasma – Atomic Emission Spectrophotometric (ICP-AES), method which simultaneously determines P, Mg and Ca with required precision and accuracy.

4.4.2 Determination of orthophosphates:

Ortho-, di-, tri- and polyphosphates can be separated by ion chromatography using a specific anion exchange column. Use of a conductivity detector provides a way for their detection as well as quantitation. Sponsor submitted data on ortho and triphosphates in MDHDP using an ion chromatographic method which is recommend by the Committee for their determination.

4.4.3 Determination of lead, arsenic, cadmium and aluminium:

Impurities such as lead, arsenic, cadmium and aluminium are determined by Atomic Absorption Spectrophotometry (AAS) or ICP-AES. AAS (electrothermal technique) provides for the determination of lead and cadmium which are present in low concentrations. ICP-AES can be used for the determination of aluminium. Sponsor provided data using ICP-AES method for the determination of above contaminants except for cadmium using AAS (Zeeman furnace). However, the Committee recommends AAS (Electrothermal technique) for the determination of lead and cadmium; AAS (hydride generation technique) for arsenic and ICP-AES technique for aluminium as they are sufficiently sensitive and determine their levels well below the maximum levels set in the specifications monograph for MDHDP.

4.4.4 Determination of fluoride:

The sponsor has provided data on fluoride using a spectrophotometric method. The method uses distillation of fluoride as hydrogen fluoride, followed by a reaction with Ce^{+3} and Alizarin to form a red coloured chelate. The characteristic blue colour of the chelate provides for the determination of fluoride. However, the Committee recommends the use of a more specific ion selective electrode method.

4.4.5 Determination of sodium and potassium:

Sodium and potassium, either present in the raw materials or intentionally added to MDHDP, are determined by AAS-flame technique.

4.4.6 Determination of loss on ignition:

Loss on ignition of MDHDP is determined at 800 °C, 30 min.

4.4.7 Determination of particle size distribution by Laser-scattering technique:

The particle size distribution is measured by laser-scattering instrument (Horiba LA-950V).

5. Functional uses

5.1 Technological functions

MDHDP has the potential as a raising agent in certain bakery applications, either singly or in combination with other raising agents. Baking performance of raising agents is evaluated using two parameters as below:

(a) Neutralization Value (NV) is one of two important properties for a leavening agent (acid). The value describes the amount of acid required to neutralize 100g of sodium bicarbonate, the common carbon dioxide source in chemical leavening. It is a reference value, specific for each type of leavening (raising) agent (acid). The higher the NV, the less leavening acid is needed. It is therefore desirable to have a high NV to reduce the amount of leavening acid. However, higher NV usually occurs with a quicker reaction. An exception is sodium aluminium phosphate.

$$Neutralisation\_Value = \frac{amount\_of\_sodium\_bicarbonate[g]}{amount\_of\_raising\_agent[g]} x100$$

(b) Rate of Reaction (ROR): It is an efficiency test concerning a desired baking property in the industrial use of raising agents. The value describes the speed of the release of carbon dioxide (providing volume) during the leavening reaction under defined conditions. The speed or dynamic of a reaction is important in industrial preparation of baked goods. Benching and preparation time and baking conditions must be very strictly controlled otherwise the output may vary from a defined standard in colour, volume or texture and may differ from final customer expectations in a certain product. The performance of MDHDP, in terms of its NV and ROR along with other additives, is presented in Table 3:

Table 3: Baking properties of Food Additives

Food Additive	NV	ROR
Sodium aluminium phosphate, acidic	100	22
Sodiumaluminium phosphate, basic	100	10
Calcium dihydrogen phosphate	83	60
Tartaric acid	112	70
Glucono delta-lactone	45	30
Monopotassium phosphate	45	66
MDHDP	70-73	10-30

The data on neutralisation value (NV) and rate of reaction (ROR) further supports its suitability as a raising agent in other baking applications. From the above data, MDHDP may reduce the ROR compared to other organic acids or their salts indicating its suitability as a retarded raising agent. MDHDP can be produced to yield a less strongly retarded raising agent or more strongly retarded raising agent, depending on the exact production conditions with optimum neutralisation value and a range of ROR as well as controlled particle size distribution. MDHDP could be an alternative material to replace the commonly used sodium acid pyrophosphate (INS 450 (i)).

5.2 Food Categories and Use Levels

The individual proposed use levels for MDHDP are summarized in Table 4

Table 4: Proposed uses of MDHDP

GSFA Food category	*Category name (restriction)*	*Maximum level*	*Typical use level*
6.2.1	Flours (Self-raising flour)	7 g/kg (as P)	6 g/kg (as P)
6.4.2 6.4.3	Dried and pre-cooked pastas and noodles and like products	1 g/kg (as P)	0.5-1 g/kg (as P)
6.6	Batters	5.6 g/kg (as P)	4-5 g/kg (as P)
6.7	Pre-cooked or processed rice products, including rice cakes (puffed products)	6 g/kg (as P	4-5 g/kg (as P)

7.1.1 7.1.2 7.1.3 7.1.6	Bread and rolls (non-yeast-raised only products, crackers, bagels, tortillas, and premixes of those)	7 g/kg (as P)	4-5 g/kg (as P)
7.2	Fine bakery wares	7 g/kg (as P)	5.5-6.5g/kg (as P)

6. Reactions and Fate in Food

MDHDP is added to bakery wares, batters or other foods where leavening is needed; as an acidity regulator in bakery wares (this function normally equates to "raising agent", but sometimes the terms "acid", "acidity regulator" or "stabilizer" are used). MDHDP also serves as a retarded raising agent, neutralizing the caustic bicarbonate source. The reaction in foods with bicarbonate sources, such as sodium or potassium bicarbonate is shown below:

$$MgH_2P_2O_7 + 2NaHCO_3 \rightarrow MgNa_2P_2O_7 + 2CO_2\uparrow + 2H_2O$$

A secondary reaction is a partial hydrolysis of the diphosphate to monophosphate:

$$MgNa_2P_2O_7 + H_2O \rightarrow Na_2HPO_4 + MgHPO_4$$

This reaction has a mild influence on the pH value of the food matrix. A slight drop in the pH occurs during the baking process, which has an influence on the natural browning (Maillard reaction) during the baking process. This effect is normally considered by formulators by adding sodium bicarbonate in an adequate dose ("neutralizing value", NV), which is individual for each leavening agent (acid).

6.2 Stability and Degradation/Reaction Products

MDHDP has been subjected to accelerated storage studies (40°C and 75% RH). A slow, naturally occurring hydrolysis reaction can occur where magnesium dihydrogen diphosphate, in presence of water, gets converted into monomagnesium phosphate under accelerated conditions $MgH_2P_2O_7 + H_2O \rightarrow Mg(H_2PO_4)_2$.

An increase of absorbed water may results in a less retarded raising action and leads to deviations of the baking volume by using same quantity of additive. The result of total hydrolysis leading to the formation of monomagnesium phosphate, but likely outside the specified limits No other reactions are expected to occur.

REFERENCES

[1]Chemische Fabrik Budenheim KG, Magnesium dihydrogen diphosphate, INS 450 (ix), Dossier submitted to the JECFA Secretariat, December, 2011.

[2]FAO/WHO. (1982), Technical report series 683, Evaluation of certain food additives and contaminants (Twenty-sixth report of the Joint FAO/WHO Expert Committee on Food Additives) (p. 13). Geneva: World Health Organisation.

[3]Food Chemicals Codex, 8th Edn. (2012), National Academy Press, Washington DC

[4]Combined Compendium of Food Additive Specifications, FAO JECFA Monographs 1, Vol. 4, 2006