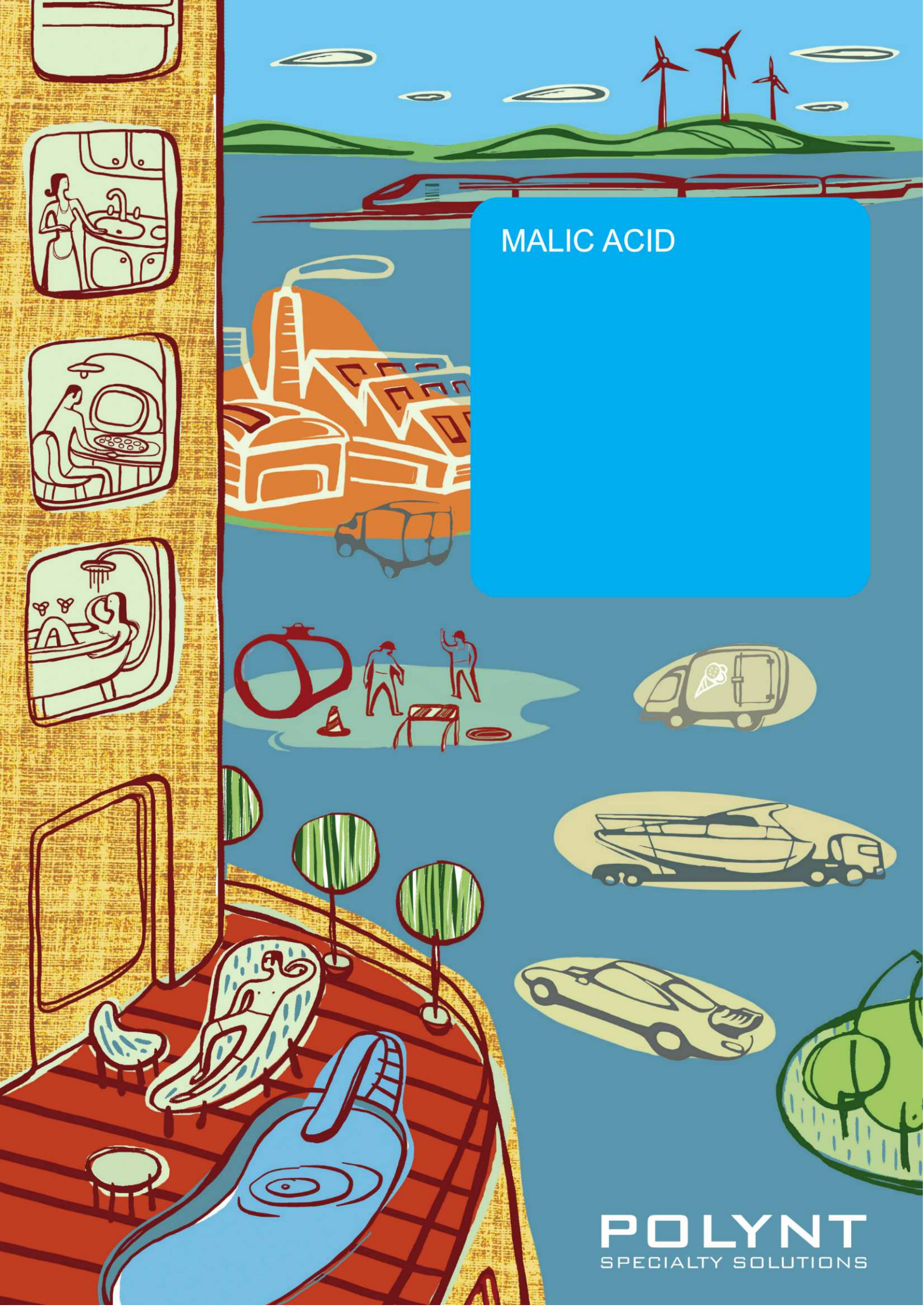




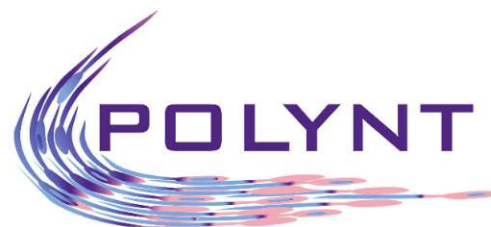
## MALIC ACID

**POLYNT**  
SPECIALTY SOLUTIONS



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- Properties and Advantages of Malic Acid
- Application of Malic Acid
- Legislation
- Safety and Hygiene
- Chemical and Physical Properties
- Integrated Management System





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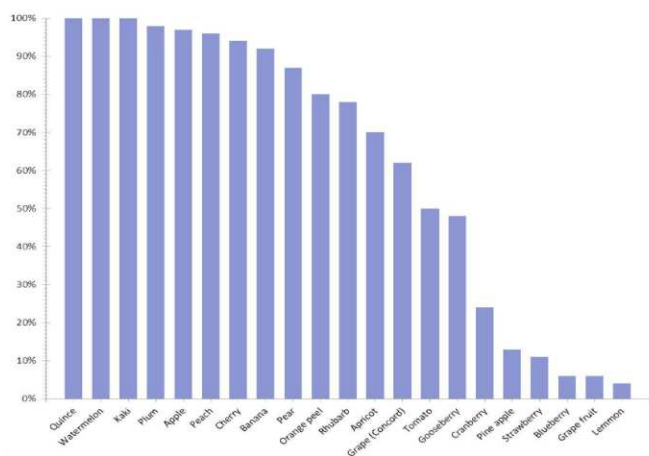


Fig.1 Malic Acid in Fruits and Berries (Malic as percentage of total acids)

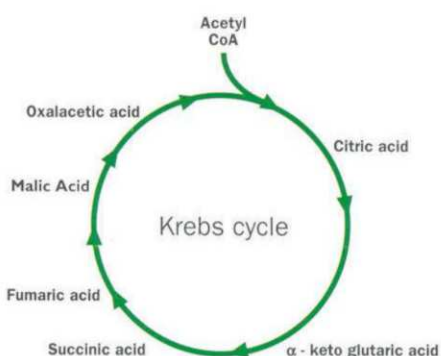


Fig.2 Krebs Cycle

## General information

Malic Acid is manufactured by Polynt SpA by hydration of Maleic Anhydride (at high temperature and pressure) in its factory of Scanzorosciate (Bergamo), in a modern production plant with 13 .000 tons/year capacity. Malic Acid is widely found in nature and is the predominant organic acid in many fruits and berries, far more than citric acid (Fig.1).

In the animal kingdom and in humans too, Malic Acid plays an essential role in carbohydrate metabolism and, therefore, in the production of basic energy for cellular processes. It is, in fact, the precursor of oxalacetic acid and an important step in the Krebs cycle (Fig.2). Malic Acid cristallizes from aqueous solutions as white, translucent crystals which are anhydrous, nonhygroscopic (in normal conditions) and non-volatile, with a melting point of about 130°C. Its first dissociation constant ( $K_1 = 4.0 \times 10^{-4}$  at 25°C) (Fig.3) gives to malic

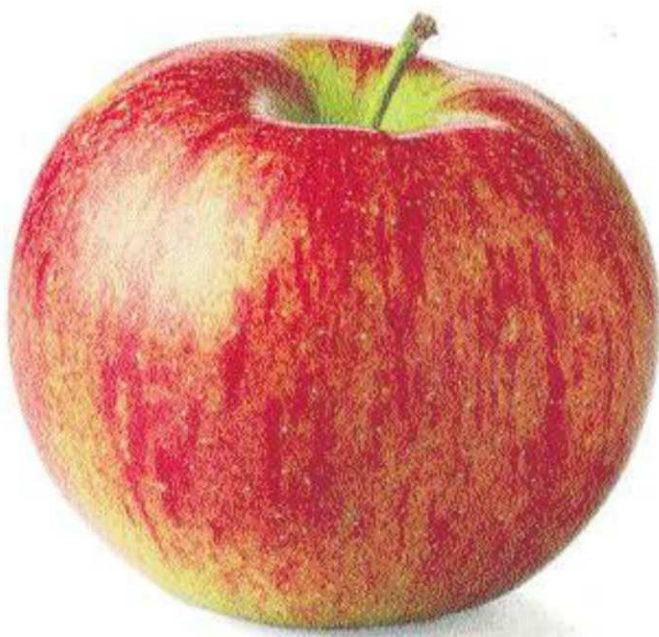
acid relatively strong acidic properties, strong enough in solution to give a fairly high hydrogen ion concentration, but, at the same time, weak enough to create an effective buffer solution.

By comparing the buffering index of the most common food organic acidulants, it is clear that the Malic Acid index rates is high (certainly higher than that of citric acid) and it is well known that bigger value, means better buffering action of the acid.

|                   |             |
|-------------------|-------------|
| Tartaric acid     | 3.53        |
| Fumaric acid      | 3.46        |
| <b>Malic acid</b> | <b>3.26</b> |
| Adipic acid       | 3.26        |
| Succinic acid     | 2.90        |
| Citric acid       | 2.46        |

### Buffering indices

Malic Acid has a very good solubility in water: at 25°C the saturated solution contains 58% of Malic Acid by weight and its solubility grows very rapidly when the temperature is increased (Fig.4).



## Properties and advantages of Malic Acid

### Flavour enhancement

Malic Acid blends very well with a wide range of essences and flavours; its acid taste builds up slowly at the beginning, but lasts for a very long period.

On the other hand, with citric acid, the acid taste builds up more rapidly, but taste stimulation is of short duration (Fig.5).

The final effect of this is to give the sensation, in case of Malic Acid of a stronger taste and this property makes Malic Acid particularly desirable in the formulations of many beverages.

### Storage prolongation

Since Malic Acid is anhydrous and non-hygroscopic, it can be stored, in normal conditions, for a long time without any caking issues. Thanks to this characteristic the end products, in powder or in granular form, blended with Malic Acid also have a longer shelf life.

### Advantage of a lower melting point.

The melting point of Malic Acid is about 130°C, a temperature clearly lower than that of citric acid (153°C).

This difference is particularly interesting and important, especially in the production of hard candies.

### Better solubility of its salts

The calcium salts of Malic Acid are much more soluble in water compared with those of citric acid (Fig.6), avoiding cloudiness in the end products even when only moderately hard water is used.

### Chelating power

Malic Acid has good chelating properties which permit the formation of stable complexes with many heavy metals. In view of this property Malic Acid can replace citric acid in the processing and refining of edible oils as well as in protection against food deterioration.

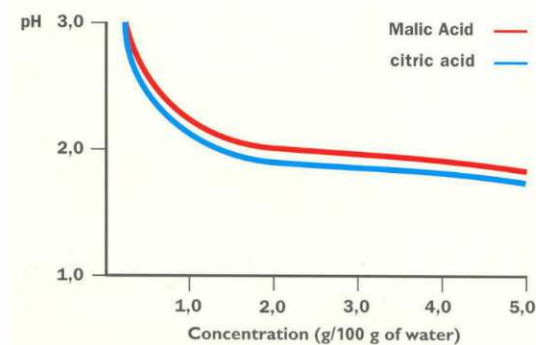


Fig.3 pH of aqueous solutions at 25°C

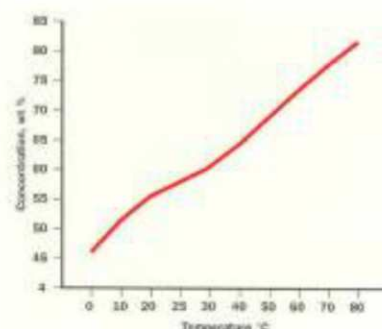


Fig.4 Solubility of Malic Acid in water

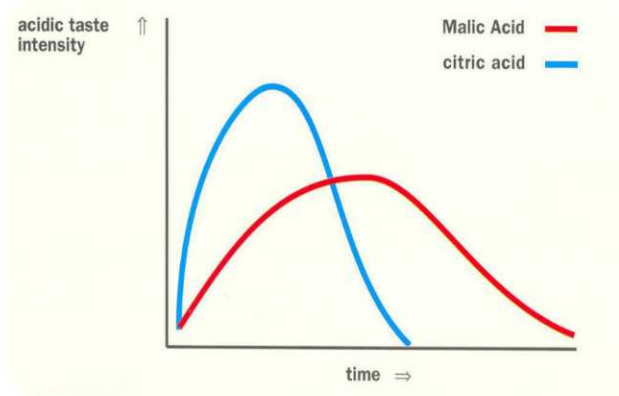


Fig.5 Taste retention curves of Malic and citric acid

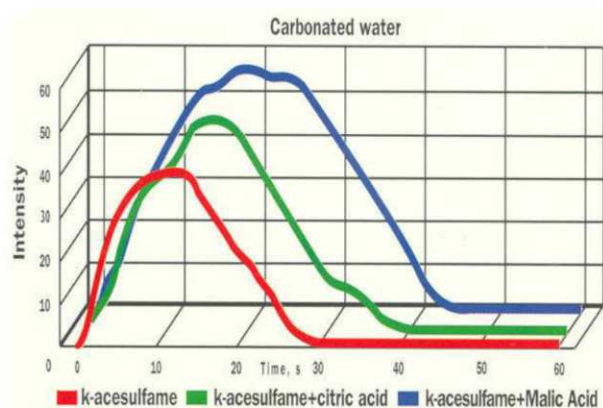


Fig.7 Sweetness

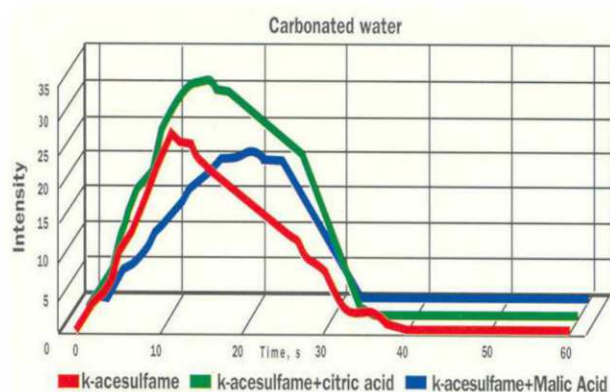


Fig.8 Bitterness

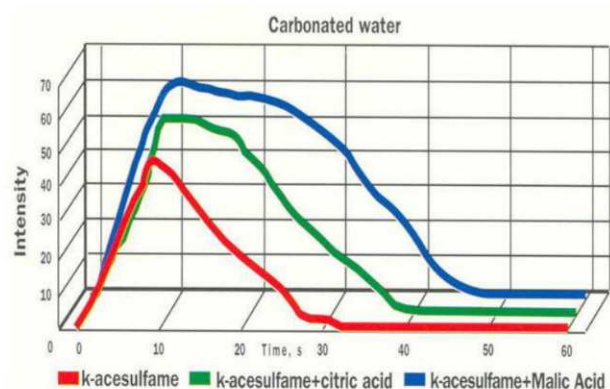


Fig.9 Fruitness

Maximum concentration in aqueous solution at room temperature

Solubility of calcium salts at room temperature

g/100 g solutions

g anhydrous salt/100 g water

|               |       |      |
|---------------|-------|------|
| Citric acid   | 64.0  | 0.09 |
| Malic Acid    | 58.0  | 0.30 |
| Tartaric Acid | 125.0 | 0.30 |
| Succinic acid | 6.5   | 1.28 |
| Lactic acid   | 100.0 | 3.50 |

Fig.6 Solubility

### Synergy with artificial sweeteners

Recent studies have shown that the longer taste retention of Malic Acid helps to mask the bitter aftertaste of many artificial sweeteners, enhancing in the meantime sweetening power. The following three points, which are some of the results obtained in a study carried out by the Experimental Station for the Food Preservatives Industry of Parma on behalf of Polynt SpA, confirm without any doubt that Malic Acid:

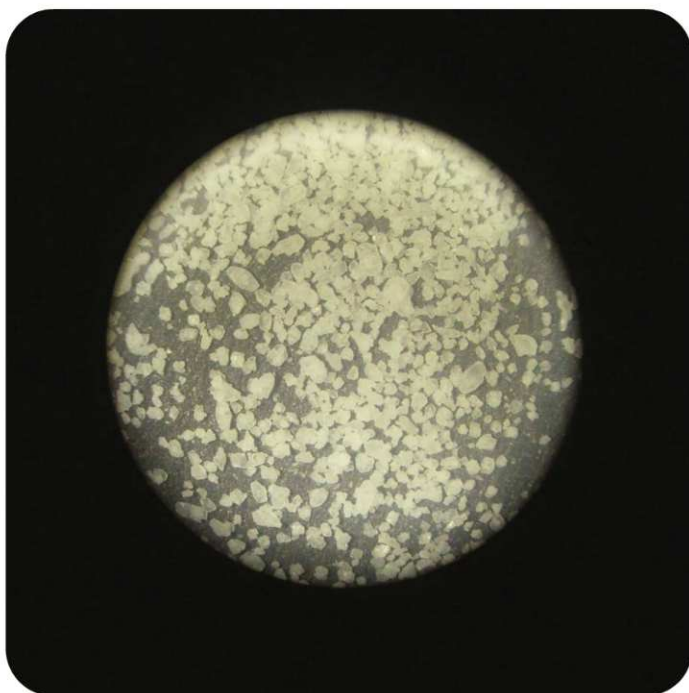
- enhances the sweetening power of Aspartame and this action is even more marked in the case of K-acesulfame (Fig.7);
- masks the inevitable bitter aftertaste that is generally present in artificial sweeteners and particularly in K-acesulfame (Fig.8);
- increases the efficacy of flavouring agents (Fig.9).

### Greater economy

The use of Malic Acid, in substitution for or combination

with citric acid, has the following advantages:

- Food technology studies confirm that by using Malic Acid it is possible to achieve the same acid taste as with citric acid, but with a smaller quantity. This is attributable to the longer taste retention of Malic Acid and in the final analysis, to its stronger taste. Experiments have demonstrated these facts, by showing that with a wide range of foods and beverages the same acid taste obtained with anhydrous citric acid can be achieved by using about 10% less Malic Acid (as compared with about 20% for monohydrate citric acid).
- The ability of Malic Acid to enhance and to strengthen, the effect of flavours and fragrances, very often makes it possible to reduce their quantities, so achieving a significant saving.
- In the case of formulations containing artificial sweeteners (like low calorie beverages), the synergic effect of Malic Acid quite often enables smaller quantities to be used.



#### Polynt SpA Malic Acid grades:

- granular
- fine granular
- special fine granular
- powder

*Malic Acid powder particles  
(photo taken under  
electronic microscope -  
SEM)*

## Application of Malic Acid

Thanks to its properties, Polynt SpA Malic Acid, has a wide range of applications in the food industry (beverages, candies, chewing gums, jellies, jams, frozen confectionery), animal foodstuffs (petfood, mixtures of acidifiers for pigs), treatment of metals, metal plating, pharmaceutical and cosmetic industry and in building materials.

### Beverages

Malic Acid is increasingly used in both liquid beverages and powder drinks as a flavour enhancer, because of its buffer power and to increase the efficacy of antimicrobial preservatives. Due to its acid taste, which is stronger than that of citric acid, Malic Acid is frequently used as a substitute for or in combination with it in the formulation of beverages, thus substantially contributing to intensify and improve the taste of the fruits flavours used.

- In sports drinks and in their derivatives, "life style" drinks, and in enriched drinks, which

are very often rich in calcium salts. Polynt SpA Malic Acid always enable to obtain clear solution, without any undesirable cloudiness, thanks of the high solubility of its salts.

- In low calorie drinks, Polynt SpA Malic Acid is increasingly used to mask the unpleasant aftertaste of many artificial sweeteners, thanks to its longer taste retention, which makes the final flavour much smoother and more balanced. This synergy between Malic Acid and synthetic sweeteners makes possible a reduction in the quantity of sweetener required, with a substantial cost savings. Moreover, it must be underlined that, by replacing citric with Malic Acid, 10-20% on the acidulant can be saved.

- Powdered drinks containing Malic Acid instead of other acidulants, such as citric acid, can be stored longer without any caking issues since it is anhydrous and non-hygroscopic.





- In wine production, the right acidity of the must is essential, not only to control the fermentation process, but also the flavour obtained through ageing. The use of Malic Acid, citric acid or tartaric acid for the pH adjustment before and after fermentation, is strictly controlled to a greater or lesser degree by the laws of individual countries, which must comply with when the acidulant to be used is chosen. An additional advantage in using Malic Acid comes from its ability to form stable iron chelates that prevent the precipitation of iron salts, which in many cases, are the main cause of cloudy wine.

- The production of branded cider, in which the organoleptic properties must remain absolutely constant, requires a high level of standardization of the production method and of starting materials both. The apple juice, used as a starting product, has to contain a predetermined percentage of sugar and a constant acidity, which is not always achievable without the addition of acidulants. In fact, the natural acidity of apples can vary, even

considerably, during the year as well as depending on where the apples come from. In view of the fact that Malic Acid is the main natural acid contained in this fruit, it is the ideal acid to make up for any natural acidity deficiency.

Moreover malo-lactic fermentation occurs concurrently with the alcoholic fermentation. This is generally considered to be undesirable and necessitates the addition of Malic Acid to restore the characteristic organoleptic properties of the end product.

#### **Confectioneries**

- In candies or sweets, the use of Malic Acid is preferable to other acidulants because its melting point is lower. Especially in hard candies this a key factor, since the acid can easily be incorporated in the cooked syrup on the slub. Moreover, since the temperature to be reached is rather low, it is possible to avoid caramelization and minimize sugar inversion. Malic Acid is also used in soft and effervescent candies.



In the latter case the Malic Acid blends with the coating of the candy together with other ingredients.

- In chewing-gums, Malic Acid, combined with saccharine, improves saliva stimulation. Moreover by using mixtures of acids with different solubility rates it is possible to make chewing-gums whose taste is more or less prolonged. In this case, the synergism between Malic Acid and artificial sweeteners, offers the same advantages we have seen previously in other categories of products.

#### **Desserts**

- Acidulants are used in the production of many different kind of desserts: for instance, ices, sherbets, variegated ice creams, jelly dessert powders, milk puddings etc . Depending on the final product, Malic Acid is used to enhance the taste of the fruit flavours (as in ices and sherbets) or as a pH adjuster in order to obtain the right gelling rate, Jams and Fruit Jellies. Malic Acid is added in these products to compensate for any deficiencies in natural acid

contained in the fruit. Generally speaking, about 0.5% is enough to obtain a pH that will enable pectin to perform its jelling function correctly and effectively. Obviously, the properties of the Malic Acid are also used to enhance the taste of the fruit. In the case of low-calorie jam, in which an artificial sweetener is used, Malic Acid has the same function as in low-calorie drinks.

#### **Fruit and Vegetables**

In the conservation of fruit and vegetables, whether fresh or canned, the use of acidulants is of fundamental importance.

- Canned fruit and vegetables, During sterilization, the pH needs to be lower than 5 to enable a mild heat treatment to be used (lower temperature and shorter treatment). Indeed, with a pH exceeding 5, it would be necessary to operate at higher temperatures, which, apart from destroying the micro-organisms, would also destroy the natural structure of the products, leading to deterioration in their appearance and consistency





and a reduction in their nutritional value. The pH is kept under control by means of a food organic acid, and Malic Acid, since it also enhances flavour, is the best one for the purpose. Fruit and vegetables prepared for canning or freezing very quickly become dark due to the oxidizing action of the air. This can be partially or totally avoided by the addition of ascorbic acid. The combined use of Malic and Ascorbic Acid has a synergic effect and increases the effectiveness of the latter.

- Fresh vegetables.

Many vegetables, for example green salads, if treated with solutions containing a preservative and an acidulant such as Malic Acid, will maintain fresh longer.

#### **Edible Oils and Fats**

In products of this type, Malic Acid has a synergic effect on the anti-oxidants used to prevent the products from becoming rancid. In addition, during the processing and refining of oils,

its chelating properties will eliminate traces of metals.

#### **Petfoods**

Malic Acid is used in pre-cooked foods for cats and dogs to obtain the pH required for jelling. Moreover Malic Acid improves the flavour which is a very important point especially in the case of cats-food. Recent studies have shown that Malic Acid added to petfoods prevents and even treats urinary calculosis, a quite frequent disease in cats and dogs.





### Pharmaceutical and Cosmetic Products

The use of Malic Acid is worthwhile in this area, because of its ability to enhance the effect of the aromas used to mask the undesirable tastes and smells of medicinals. It is also used in effervescent powders and tablets.

In the area of cosmetics, Malic Acid, likewise other alphanhydroxy acids, applies in creams to prevent wrinkles.

### Industrial Uses

The use of Malic Acid is increasing in a wide range of industrial applications as follow:

- In the treatment of metals such as pickling and descaling, as a substitute for strong inorganic acids, since it has the advantage of being neither corrosive nor toxic. Malic acid is also easily and fully biodegradable.

- In the food industry, especially in the manufacture of drinks, the excellent solubility of its calcium salts make it useful for removing

lime deposits from plant and equipment.

- In the textile industry, as a substitute for acetic or formic acid, since it does not damage or corrode machinery. Malic Acid also has the advantage that does not generating any unpleasant smell. It may also be included in the chemicals used in textile finishing.

- In animal feed, it is used in combination with other acids, for the acidification of pigs feed.

- In plating industry, it is used to correct the pH in plating baths.

- In the manufacture of plasters and cements it is used for the building industry, combined with tartaric acid, as a setting retardant.

*Note:* data and information here above mentioned, have to be considered as general a guidelines and the parameters have to be necessary adjusted to each need and relative end products.





## Legislation

### Chemical and Physical Properties

|                                           |                                                                     |
|-------------------------------------------|---------------------------------------------------------------------|
| Chemical description                      | Malic Acid<br>(hydroxybutanedioic acid<br>hydroxy-succinic acid)    |
| Molecular formula                         | $C_4H_6O_5$                                                         |
| Structural formula                        | $  \begin{array}{c}  HO-CH-COOH \\    \\  CH_2-COOH  \end{array}  $ |
| Appearance                                | White crystalline powder or acid-tasting granules                   |
| Molecular weight                          | 134.09                                                              |
| Equivalent weight                         | 67.05                                                               |
| Melting point                             | 130-132°C                                                           |
| $d_4^{20}$                                | 1.601                                                               |
| Dissociation constants                    | $K_1=4 \times 10^{-4}$ $K_2=9 \times 10^{-6}$                       |
| pH of aqueous solution                    | (see curve in Figure 2)                                             |
| Combustion heat (20°C)                    | 320 kcal/mole                                                       |
| Heat of solution                          | -4.9 kcal/mole                                                      |
| Viscosity at 20°C (50% aqueous solution)  | 6.5 CP                                                              |
| Solubility in water                       | (see curve in Figure 4)                                             |
| Solubility in ethanol (g/ 100 ml at 25°C) | 39.16                                                               |
| Buffer index                              | 3.26                                                                |

### Microbiological Data

|                 |           |
|-----------------|-----------|
| Bacteria        | <10 CFU/g |
| Yeasts          | <10 CFU/g |
| Moulds          | <10 CFU/g |
| Total coliforms | <10 CFU/g |
| Salmonella      | absent    |

In the United States, Malic Acid is considered harmless by the FDA (Food and Drug Administration), which classifies it as GRAS - that is "Generally Recognized as Safe" (the Code of Federal Regulations 21 CFR 184.1069 -1993 refers), and its use is allowed without any limitations, (except as required by good manufacturing practice) as a flavour enhancer, flavouring agent and adjuvant, and pH control agent.

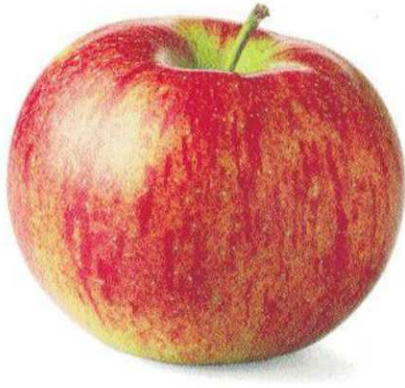
In the European Union, the directive on "Food Additives other than Colours and Sweeteners", under No. 95/2/EC of 20th February 1995, permits the general use of Malic Acid (E296) and its salts (E350, E351, E352) in the area of food processing, except for the limitations mentioned in the same directive.

In Italy, the use of Malic Acid in food processing is governed by Ministerial Decree No. 209 of 27th February 1996, which reflects the provisions of European Directive 95/2/EC.

N.B. The use of acidulants, sweeteners, or other additives mentioned in this brochure is governed by the specific legislation of individual states.

### Safety and Hygiene

In accordance with the laws of the European Union, all the safety regulations that have to be observed in using the product are contained in the relevant MSDS.



## Integrated Management Systems

In order to satisfy Customer needs and to improve the performance continually, as far as regards Health, Safety and Environment, the plant has an Integrated Management System.

1991

ISO:9002 Quality System Certification

Subscription of the "Responsible Care" program

1994

1999

HACCP Management of a Food Hazard Analysis

Quality System Certification from ISO:9002/1994 to  
ISO:9001/2000

2002

2006

ISO:14001/2004 Environmental Management System

FAMI-QS Quality and Safety System for Specialty Feed  
Ingredients and their Mixtures

2008

ISO22000:2005 Food Safety Management Systems

2011

PAS 220:2008 Prerequisite Programmes on Food Safety  
for Food Manufacturing



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