Polynt Intermediates

Malic Acid

Polynt Group Intermediates & Specialties
Malic Acid

Contents

Production Site

EMEA

Polynt S.p.A. - ITALY (Scanzorosciate)

Polynt Reichhold Group

After the merger on May 2017 the new Polynt-Reichhold Group is a global Company in the Intermediates, Coating and Composite Resins, Thermoset Compounds, Gel-coats and niche Specialties. This combination enhances the Group's leading position as a global vertically integrated specialty chemicals player, with significant global presence in Europe, North America and Asia, a strategy initiated by Polynt with the successful integration of PCCR and CCP in the last years and now further reinforced by Reichhold's global scale, extensive product portfolio and R&D competencies.

Polynt-Reichhold Group is known for its superior quality and impressive range of products and with its excellent distribution network it can provide first-class service to customers whatever their market. Customer Service and Technical Service teams are renowned for their customer focus, offering the best service even after products have left manufacturing.

The Group strives to keep customers satisfied, assisting them in producing premium quality products every time they use its products. Product innovation is important for the Group's business and it's the reason for which it constantly works with customers to find solutions to problems. Introducing new or improved products ensures that Polynt-Reichhold Group continue not only to deliver what the market wants and needs, but also when it is wanted and needed.

Malic Acid

Malic Acid is manufactured from Maleic Anhydride through an hydration reaction at high temperature and pressure in the modern Polynt SpA production plant (13,000 tons/year capacity) located in Scanzorosciate (Bergamo).
Malic Acid is widely found in nature and is the predominant organic acid in many fruits and berries (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 plays important step in the Krebs cycle (Fig.2).

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

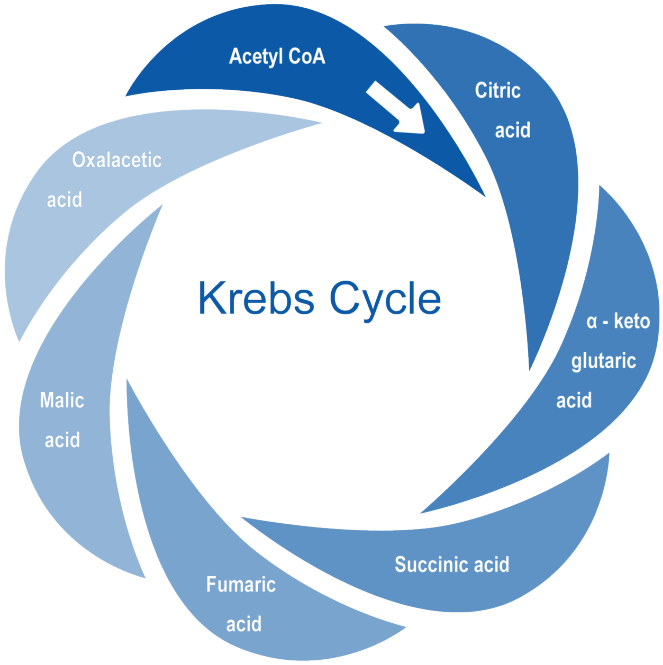


Fig.2 Krebs Cycle

Malic Acid crystallizes from aqueous solutions as white, translucent crystals which are anhydrous, non-hygroscopic (in normal conditions) and non-volatile, with a melting point of about 130°C.
Its first dissociation constant (K1 = 4.0 x 10-4 at 25°C) (Fig.3) gives 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.

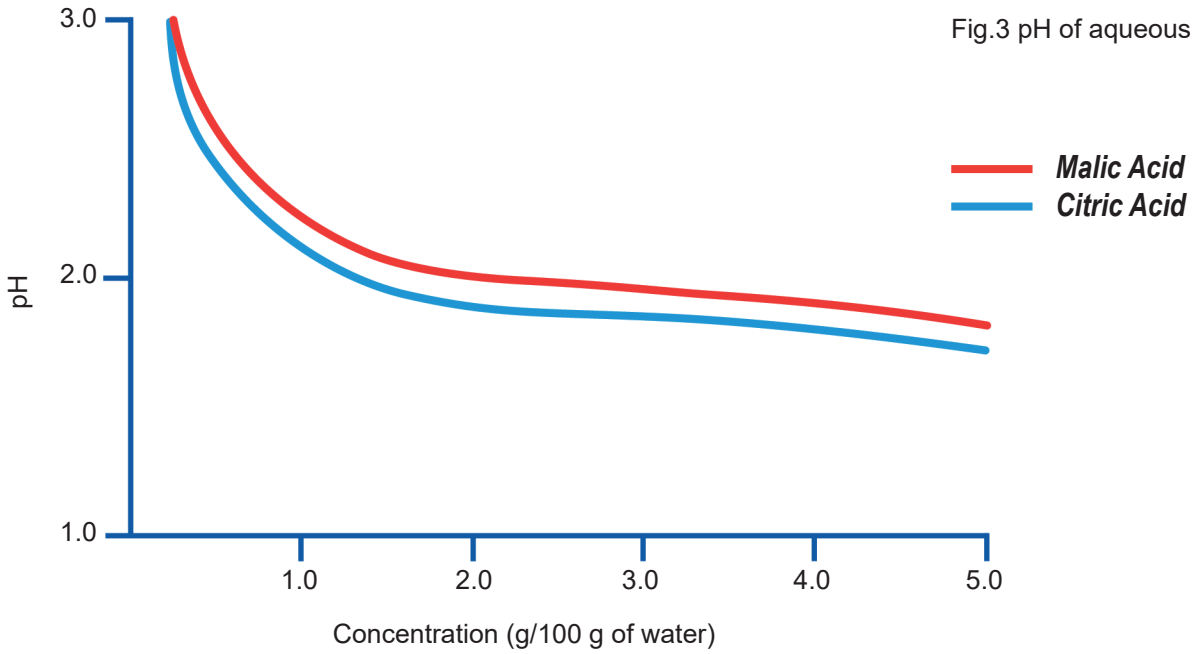


Fig.3 pH of aqueous solutions at 25°C

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

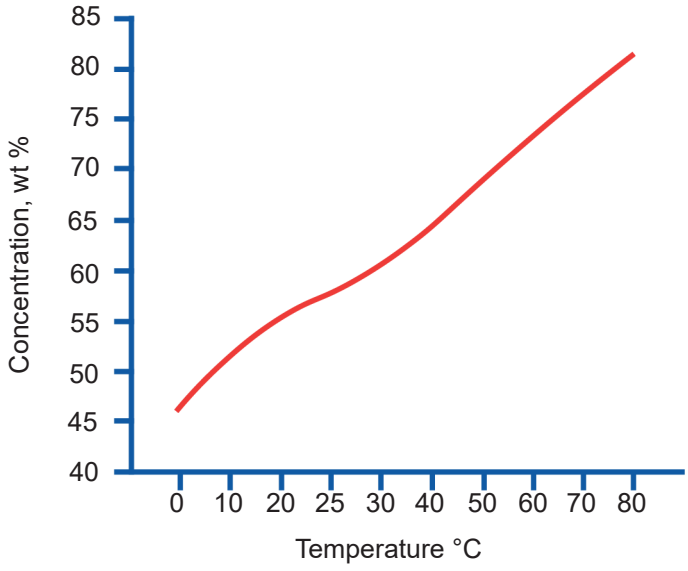


Fig.4 Solubility of Malic Acid in water

Buffering Index	
Tartaric Acid	3.53
Fumaric Acid	3.46
Malic Acid	3.26
Adipic Acid	3.26
Succinic Acid	2.90
Citric Acid	2.46

Properties and advantages of Malic Acid in comparison with Citric Acid

FLAVOUR ENHANCEMENT

Malic Acid blends well with a wide range of essences and flavours; the acidic taste builds up rapidly, but taste stimulation is short lived (Fig. 5). The final effect of this is to give the sensation of a strong 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 long periods of 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 long 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 sweets.

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

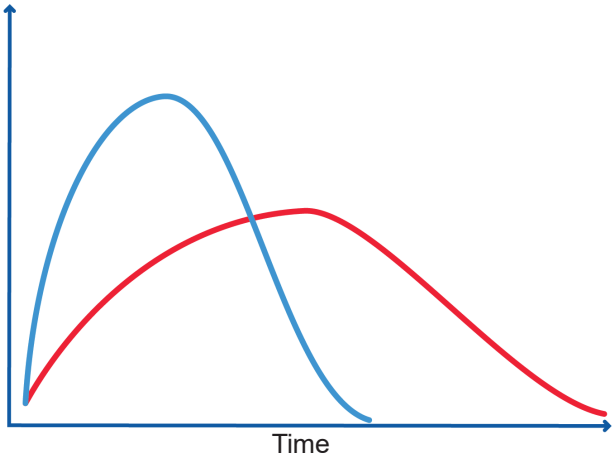


Fig.5 Taste retention curves of Malic and citric acid

Malic Acid
Citric Acid

	Maximum concentration in aqueous solution at room temperature g/100 g solutions	Solubility of calcium salts at room temperature 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 apparent 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 three important advantages.
Food technology studies confirm that by using Malic Acid it is possible to achieve the same acid taste as citric acid, but in smaller quantities. 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 acidic 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.

Fig.7 Sweetness

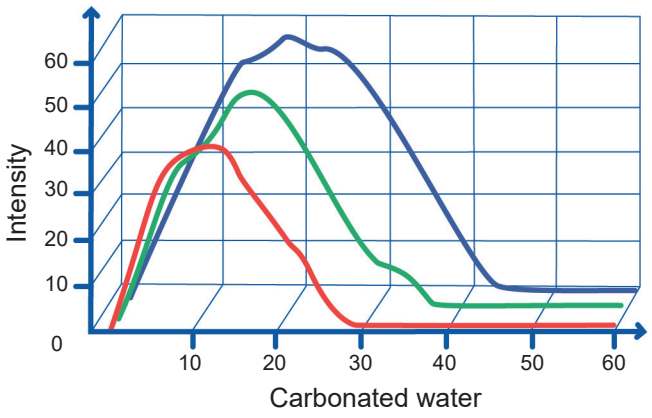


Fig.9 Fruitiness

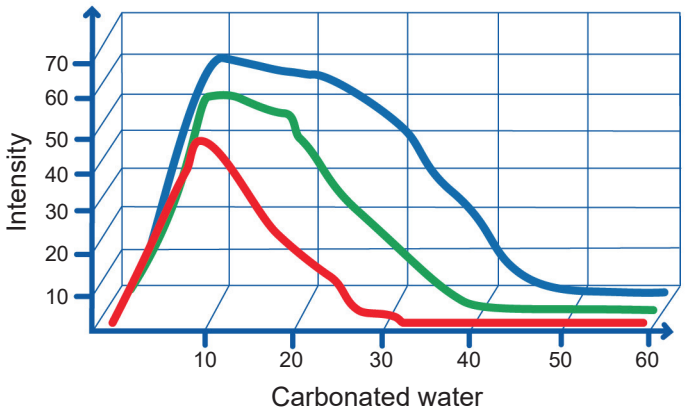
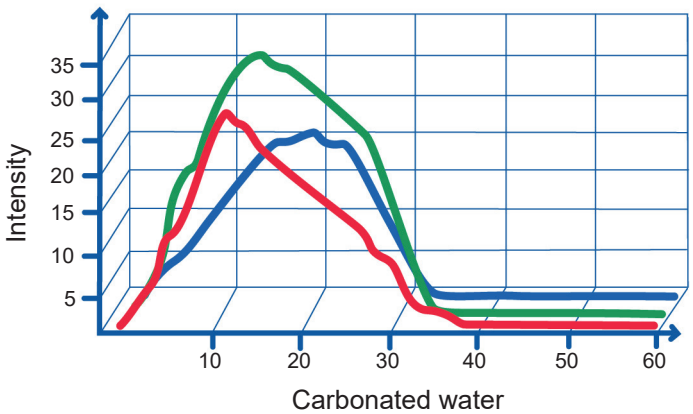
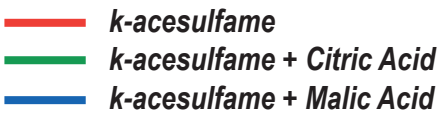


Fig.8 Bitterness





Application of Malic Acid

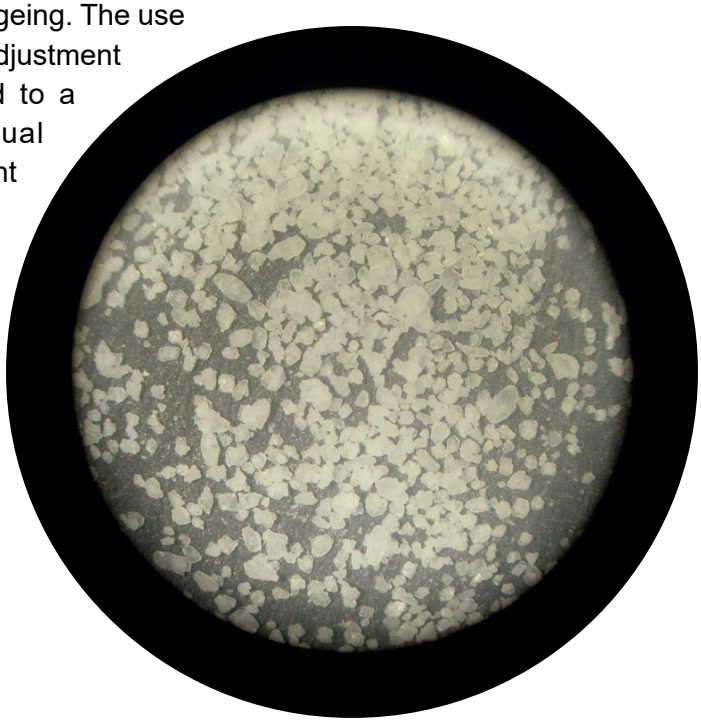
Thanks to its properties, Malic Acid made by Polynt SpA has a wide range of applications in the food industry (beverages, candies, chewing gums, jellies, jams, frozen confectionery), animal foodstuffs (pet food, mixtures of acidifiers for pigs), treatment of metals, metal plating, pharmaceutical and 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 acidic taste Malic Acid is frequently used as a substitute for/or in combination with Citric Acid in the formulation of beverages, thus substantially contribute to intensifying and improving 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's Malic Acid always enables a clear solution to be obtained, without any undesirable cloudiness, thanks to the high solubility of its salts.
In low calorie drinks, Polynt's 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 sweetheners makes it possible to reduce the quantity of sweetener used, enabling 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.

Polynt's Malic Acid grades:

- Granular
- Fine Granular
- Special Fine Granular
- Powder



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

In wine product, the correct acidity 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. 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 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 thanks to its low melting point. Especially in hard candies this is a key factor, since the acid can easily be incorporated in the cooked syrup on the slab. Also, as the required temperature is quite low, it is possible to avoid caramelization and minimise sugar inversion.
Malic Acid is also used in soft and effervescent candies.
In the case of the latter, the Malic Acid blends the coating of the candy together with other ingredients.
In chewing-gums, Malic Acid, combined with saccharine, improves saliva stimulation. By using mixtures of acids with different solubility rates, it is possible to make chewing gum with longer lasting taste.
In this case, the synergy between Malic Acid and artificial sweeteners, offers the same advantages previously seen in other product categories.

DESSERTS

Acidulants are used in the production of many different kind of desserts: for example, 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 correct gelling rate in james 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. During the sterilization, of canned fruits and vegetables, 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 most suited to this 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.
Malic Acid is also useful for fresh vegetables: many vegetables, for example green salads, if treated with solutions containing a preservative and an acidulant such as Malic Acid, maintain freshness for longer.

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 medical ingredients.
It is also used in effervescent powders and tablets. In the area of cosmetics, Malic Acid, and other alpha-hydroxy acids, applied to creams to prevent wrinkles.

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.

PET FOODS

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 pet foods prevents and even treats urinary calculosis, a frequent disease in cats and dogs. Additionally, In animal feed, it is combined with other acids, for the acidification of pigs feed.

INDUSTRIAL USES

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

- 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 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 plants 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 it does not generate any unpleasant smell. It may also be included in the chemicals used in textile finishing.
- In the 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 mentioned above has to be considered as a general guideline and the parameters must be adjusted for the requirements of the end products.

Legislation of Malic Acid

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.

The Directive 95/2/EC was repealed by Regulation (EC) No 1333/2008 of the European Parliament and of the Council of 16 December 2008 on food additives. Malic Acid in included in Annex II and Annex III of such a Regulation according to Regulation No. 1129/2011 and Regulation No. 1130/2011 respectively.
Malic Acid meets the provisions of Regulation No.231/2012 laying down specifications for food additives listed in Annex II and Annex III to Regulation No. 1333/2008. Malic Acid is included in Regulation (EU) No. 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food with Ref. No. 19965 and 65020.

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 Health, Safety and Environment are concerned, the plant has an Integrated Management System.

Certifications

1991	ISO:9002 Quality System Certification
1994	Subscription of the “Responsible Care” program
1999	HACCP Management of a Food Hazard Analysis
2002	Quality System Certification from ISO:9002/1994 to ISO:9001/2000
2006	ISO:14001/2004 Environmental Management System
2008	FAMI-QS Quality and Safety System for Specialty Feed Ingredients and their Mixtures
2010	Quality System Certification from ISO:9001/2000 to ISO:9001/2008
2011	ISO22000:2005 Food Safety Management Systems PAS 220:2008 Prerequisite Programmes on Food Safety for Food Manufacturing
2014	FSSC 22000
2017	Quality System Certification from ISO:9001/2008 to ISO:9001/2015
2018	Environmental Management System from ISO:14001/2004 to ISO:14001/2015

Chemical and Physical Properties

Chemical description	Malic Acid (hydroxybutanedioic acid hydroxy-succinic acid)
Molecular formula	$C_4H_6O_5$
Structural formula	HO--CH--COOH I CH_2--COOH
Appearance	White or nearly white crystal
Molecular weight	134.09
Equivalent weight	67.05
Melting point	128 - 132 °C
d^{20}_4	1.601

Chemical description	Malic Acid (hydroxybutanedioic acid hydroxy-succinic acid)
Dissociation constants	K1=4 x10-4 K2=9 x10-6
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 mPa.s
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

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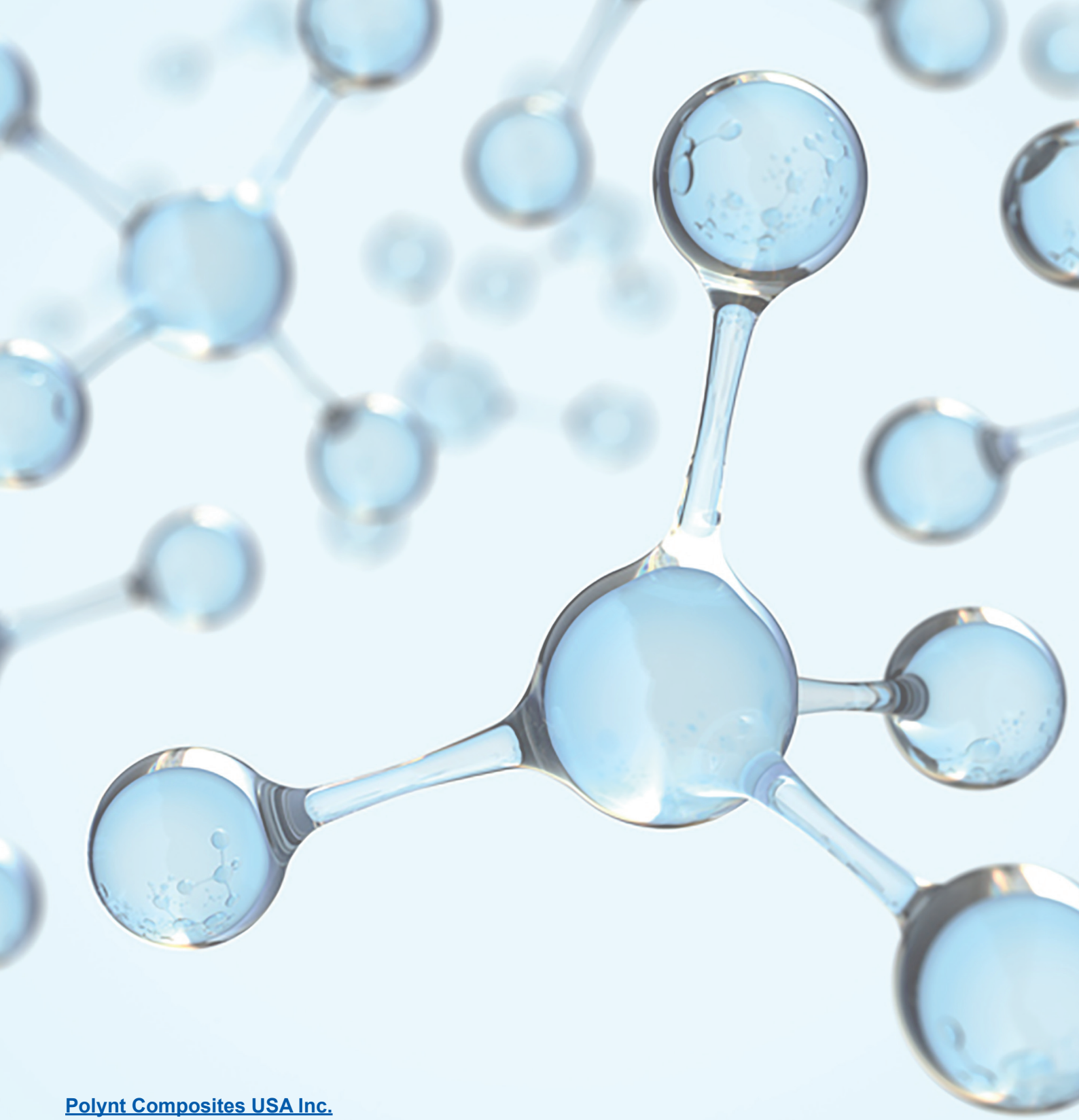

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