Nortem® Biotechnology

# Annex. Exposure Scenarios Citric Acid

| Identified use | Sector of Use - main user groups (SU) | Sector of Use – sectors of end-use | Preparation Category (PC) | Process category (PROC) | Article category (AC) | Environmental Release Category (ERC) |
|---|---|---|---|---|---|---|
| Manufacture | SU3 | SU8 | PC19 | PROC1, 2, 3, 8b | - | ERC1 |
| Intermediate | SU3 | SU8, SU9 | PC19 | PROC1, 2, 3, 4, 8b | - | ERC6a |
| Formulation | SU3, 10 | SU5, SU13, 20 | PC0, 1, 3, 9, 12, 18, 30, 31, 35, 39 | PROC 2, 3, 4, 5, 7, 8a, 8b, 9, 13, 14, 15, 19 | | ERC1, 2, 3, 4 |
| Personal care products | SU21, SU22 | SU20 | PC2, 39 | PROC 10, 11, 19 | AC8 | ERC 8a, 11a |
| Detergent and cleaning products | SU3, SU21, SU22 | - | PC3, 28, 31, 35, 36, 37 | PROC1, 2, 4, 5, 7, 8a, 8b, 9, 10, 11, 13, 19 | AC8<br>AC35 | ERC2, 4, 8A, 8D, 9A, 9B |
| Paper industry | SU3 | SU6 | PC26 | PROC 5, 8a | - | ERC4 |
| Construction products | SU3, SU21, SU22 | SU2, 10, 19 | PC10 | PROC 2, 4, 5, 7, 8a, 8b, 10, 11. 13, 14, 19, 21, 24 | AC4, 12-1, 12-2 | ERC5, 8c, 8f, 10a, 10b, 11a, 11b, 12a |
| Polymers and plastics | SU3 | SU11, 12 | PC32 | PROC 3, 5, 8a, 8b | - | ERC6b |
| Oil industry | SU3 | SU2 | PC20, 40 | PROC 3, 4, 5, 8a, 8b | - | ERC8d |
| Textile industry | SU3 | SU5 | PC20, 23, 24 | PROC 8a, 8b, 10, 13, 22 | AC5, 6 | ERC4 |
| Paints and coatings | SU3, SU21, SU22 | SU17, 18, 19 | PC9, 18, 34 | PROC 7, 8a, 8b, 10, 11, 19, 21, 24 | AC4, 11 | ERC5, 8c, 8f, 10a, 10b, 11a, 11b |
| Photography products | SU3, 21, 22 | SU20 | PC30 | PROC 5, 13 | - | ERC8a |
| Laboratory reagents | SU3 | - | PC4, 16, 20, 37 | PROC 1, 2, 4, 8a, | - | ERC4, 7 |

# Annex. Exposure Scenarios
# Citric Acid

| Identified use | Sector of Use - main user groups (SU) | Sector of Use – sectors of end-use | Preparation Category (PC) | Process category (PROC) | Article category (AC) | Environmental Release Category (ERC) |
|---|---|---|---|---|---|---|
| Water treatment | SU3 | SU14, 15, 16, 17 | PC4, 7, 14, 16, 17, 20, 25, 31, 35, 37 | PROC 1, 2, 3, 4, 7, 8a, 8b, 9, 10, 13, 18, 20, 25, xyz[1] | - | ERC4, 7 |
| Treatment of metal surfaces | SU3 | SU14, 15, 16, 17 | PC7, 14, 25, 31, 35 | PROC 2, 3, 4, 7, 8a, 8b, 9, 10, 13, 17, 18, 23 | - | ERC4, 6b |
| Agricultural applications | SU3, 21, 22 | SU1 | PC8, 12, 21 | PROC 3, 5, 8a, 8b, 10, 11, 14, 15, 19 | - | ERC2, 4, 8b, 8d |
| Medical devices | SU3, SU22 | SU20 | PC20 | PROC1 | - | ERC7 |

# Annex. Exposure Scenarios
# Citric Acid

## 1. MANUFACTURE

This document discusses only the citric acid produced for REACH-relevant applications.

Contributing activity/technique for the environment:

- Manufacture (ERC1)

Contributing activity/technique for the workers:

- Manufacture (PROC 1; PROC 2; PROC 3; PROC 8b)

Related assessment: use assessed in a joint CSR.

## 2. FORMULATION

### 2.1. Formulation and re-packing

Further description of the use:

Citric acid is formulated into a wide range of products, often at specialist formulation sites. The processes and exposures are expected to be broadly similar across different industries. Formulation is generally carried out in batch processes, which may be open or closed; several steps may be involved.

Contributing activity/technique for the environment:

- Formulation (ERC2; ERC3)

Contributing activity/technique for the workers:

- Formulation (PROC 2; PROC 3; PROC 4; PROC 5; PROC 7; PROC 8a; PROC 8b; PROC 9; PROC 13; PROC 14; PROC 15; PROC 19)

Product Category formulated:

- PC 1: Adhesives, sealants
- PC 3: Air care products
- PC 9a: Coatings and paints, thinners, paint removes
- PC 9b: Fillers, putties, plasters, modelling clay
- PC 9c: Finger paints
- PC 12: Fertilisers
- PC 18: Ink and toners
- PC 30: Photo-chemicals
- PC 31: Polishes and wax blends
- PC 35: Washing and cleaning products
- PC 39: Cosmetics, personal care products

Technical function of the substance: antioxidant; chelating agent; dispersing agent; humectant; intermediate (precursor); pH regulating agent; stabilising agent.

Related assessment: use assessed in a joint CSR.

**2.2. Use in agricultural applications**

Further description of the use:

One common method for making fertilisers involves dissolving metal sulfates in water and citric acid followed by neutralization with ammonia. This process may be carried out in an industrial setting as part of the formulation of solid or liquid fertilisers/plant feeds. In this case, citric acid is an intermediate and it is the metal-citrate or ammonium citrate that must be considered for the professional or consumer use of fertilisers/plant feeds. Magnesium citrate may be used in this context. Alternatively, mixing of fertilisers may take place on farms. In this case, exposure may be to solid or liquid citric acid or metal-citrate.

Contributing activity/technique for the environment:

- Use in agricultural applications (ERC2)

Contributing activity/technique for the workers:

- Use in agricultural applications (PROC 3; PROC 5; PROC 8a; PROC 8b; PROC 10; PROC 11; PROC 14; PROC 15; PROC 19)

Product Category formulated:

- PC 8: Biocidal products (e.g. disinfectants, pest control)
- PC 12: Fertilisers
- PC 21: Laboratory chemicals

Technical function of the substance: antiredeposition agent; antiscaling agent; intermediate (precursor); pH regulating agent.

Related assessment: use assessed in a joint CSR.

## 3. USES AT INDUSTRIAL SITE

**3.1. Formulation**

Further description of the use:

Citric acid is formulated into a wide range of products, often at specialist formulation sites. The processes and exposures are expected to be broadly similar across different industries. Formulation is generally carried out in batch processes, which may be open or closed; several steps may be involved.

Contributing activity/technique for the environment:

- Formulation (ERC4)

Contributing activity/technique for the workers:

- Formulation (PROC 2; PROC 3; PROC 4; PROC 5; PROC 7; PROC 8a; PROC 8b; PROC 9; PROC 13; PROC 14; PROC 15; PROC 19)

Product Category used:

- PC 1: Adhesives, sealants
- PC 3: Air care products
- PC 9a: Coatings and paints, thinners, paint removes
- PC 9b: Fillers, putties, plasters, modelling clay
- PC 9c: Finger paints
- PC 12: Fertilisers
- PC 18: Ink and toners
- PC 30: Photo-chemicals
- PC 31: Polishes and wax blends
- PC 35: Washing and cleaning products
- PC 39: Cosmetics, personal care products
- PC 0: Other

Sector of end use:

- SU 5: Manufacture of textiles, leather, fur;
- SU 13: Manufacture of other non- metallic mineral products, e.g. plasters, cement;
- SU 20: Health services

Technical function of the substance: antioxidant; chelating agent; dispersing agent; humectant; intermediate (precursor); pH regulating agent; stabilising agent.

Related assessment: use assessed in a joint CSR.

**3.2. Use as an intermediate in the production of other organic chemicals**

Further description of the use:

Citric acid may be used as an intermediate in the formation of:

- Metal-salts, such as magnesium citrate, iron citrate or zinc citrate.
- Others salts, for example ammonium citrate.
- Esters such as triethyl citrate or tributyl citrate.

In a typical process for the production of citrate salts, citric acid is dissolved in deionised water. Addition of a source of the other ion results in conversion of citric acid to its salt. The salt is separated by evaporation and centrifugation, then dried, sieved and bagged. The reactions may take place in a closed batch or continuous process with occasional opportunities for exposure arising, for example, during sampling.

Contributing activity/technique for the environment:

- Use of citric acid as a chemical intermediate (ERC6a)

Contributing activity/technique for the workers:

- Use of citric acid as a chemical intermediate (PROC 1; PROC 2; PROC 3; PROC 4; PROC 8b)

Product Category used:

- PC 0: Other: Intermediate

Sector of end use:

- SU 8: Manufacture of bulk, large scale chemicals (including petroleum products)
- SU 9: Manufacture of fine chemicals

Technical function of the substance: intermediate (precursor)

Substance supplied to that use: as such; in a mixture.

Related assessment: use assessed in a joint CSR.

**3.3. Detergent and cleaning products and other household products**

Further description of the use:

Citric acid and its salts are used in a wide variety of household products, as well as cleaning and maintenance products for industrial and professional uses. The large number of household products includes, but is not limited to:

- Laundry products: These include detergent powders, detergent liquids, laundry pretreatment products and fabric softeners.

- Dish washing products: These are hand dishwashing liquids and machine dishwashing products (dishwashing powders/detergents and dishwashing liquids/rinse aids).

- All purpose cleaners: These are used in cleaning hard surfaces like windows, mirrors, wood, floors and tiled walls [RIVM, 2006]. The products can be liquid cleaners, spray cleaners or wet tissue application.

- Abrasive cleaners: These are used in remove soil which is firmly attached to the surface (e.g. lavatory pan, washbasins and kitchen sink/ working top) and can be powders, liquids or scouring pads [RIVM, 2006]

- Sanitary products: These are bathroom cleaners (sprays and liquids) and toilet cleaners.

- Floor, carpet and furniture products: These are products that provide a combined effect of cleaning and polishing.

- Metal polish: Consumer or professional use of, e.g., silver polishes, either ready-to-use or solid preparations which need to be dissolved in water.

- Water treatment/scale inhibition products for household appliances.

- Vehicle care products.

The main use or function of citric acid and its salts in detergents and cleaning products is as a complexing agent/ sequestering builders to remove water hardness minerals and ‘build’ the cleaning efficiency of the surfactant. They can also function as additives (e.g. in handwashing liquids [RIVM, 2006]) or acids (e.g., in bathroom/ toilet cleaning liquids or silver polish).

Technical applications of citric acid and its salts in various industries as a complex-forming agent, cleaning agent, softening agent, decalcifying agent, de-rusting agent, corrosive agent and synergist in antioxidant mixtures accounted for 20% of the total production volume (500,000 tons/annum) in Europe (including Eastern Europe and Israel) in 1999

[HERA, 2005]. The total consumption of citric acid in household cleaning applications in the EEA (i.e., EU + Iceland, Switzerland and Norway) in 2002 was 103,000 tons [HERA, 2005].

Contributing activity/technique for the environment:

- Detergent and cleaning products and other household products (ERC4)

Contributing activity/technique for the workers:

- Detergent and cleaning products and other household products (PROC 1; PROC 2; PROC 4; PROC 5; PROC 7; PROC 8a; PROC 8b; PROC 9; PROC 10; PROC 11; PROC 13; PROC 19)

Product Category used:

- PC 3: Air care products
- PC 28: Perfumes, fragrances
- PC 31: Polishes and wax blends
- PC 35: Washing and cleaning products
- PC 36: Water softeners
- PC 37: Water treatment chemicals

Sector of end use:

- SU 0: Other: Industrial Uses

Technical function of the substance: antioxidant; antiredeposition agent; antiscaling agent; brightener; chelating agent; cleaning agent; softener.

Substance supplied to that use: as such.

Related assessment: use assessed in a joint CSR.

**3.4. Use in paper products**

Further description of the use:

Citric acid is used in the cleaning of papermaking machines and to prevent build up of deposits. Cleaning applications are covered under another exposure scenario; this scenario covers use of citrate as an additive or processing aid in the paper-making industry.

Contributing activity/technique for the environment:

- Use in paper products (ERC4)

Contributing activity/technique for the workers:

- Use in paper products (PROC 5; PROC 8a)

Product Category used:

PC 26: Paper and board treatment products

Sector of end use:

- SU 6a: Manufacture of wood and wood products

- SU 6b: Manufacture of pulp, paper and paper products

Technical function of the substance: bleaching agent; finishing agents; softener

Substance supplied to that use: as such; in a mixture.

Related assessment: use assessed in a joint CSR.

**3.5. Use in polymers and plastics products**

Further description of the use:

Citric acid may be used as a component of blowing agent in the manufacture of foamed thermoplastics. This application, described below, should be taken as representative of where and why citric acid or citrate salts may be used within the plastics and polymers industry; other applications are possible.

Polyolefin foams are used for a variety of applications such as automotive, construction, food packaging, sport and leisure, and many other industrial and consumer uses. They usually havea high strength to weight ratio and are manufactured in a variety of processes and in low density (25 - 250 kg/m3) or high density (250 - 700 kg/m3) versions, or even in densities as low as 16 kg/m3 for polystyrene. All current extrusion processes involve the following steps: melting, mixing with blowing agents, cooling of melt, expansion and degassing/aging. The steps in this process can be realized in different configurations of equipment, e.g., with long single-screw extruders, twin-screw extruders, or tandem extruder lines. The choice of chemical or physical blowing agents depends on the foam density to be reached (e.g. the foam application) and influences the necessary foaming equipment and the costs of the foamed materials. High-density thermoplastic foams based on, e.g., polypropylene or polystyrene, may be produced using blowing agents which decompose to generate gas which is soluble in the melt but which is released as the pressure is reduced (e.g., by passing through a dye) to produce a foam. The foaming process is complex but involves bubble nucleation followed by bubble growth.

One example of a commercially used chemical foaming agent is based on citric acid (or monosodium citrate) in combination with sodium carbonate or (sodium bicarbonate) in a weight ratio of between about 1:1 and about 5:1 respectively [US 5,302,455]. The citric acid/sodium bicarbonate system decomposes at 160 – 210°C to release 120 cm3/g of CO2. [Karger-Kocsis, 1999; Brydson, 1999; Holmberg, 2002].

Both citric acid (or citrate salt) and (bi)carbonate may be surface-treated with, for example, a fatty acid ester to make them compatible with the polyolefin. A concentrated master batch of the formulated foaming agent in polymer at loading levels of from about 5% to about 50% actives may then be prepared. The master batch is added to the polymer melt which is to be foamed such that the blowing agents are at 0.1 to 2.0% active levels in the final formulation [US 5,302,455 and refs. therein]. The pre-treatment formulation and foaming processes are typically closed or open batch processes. The citrate is typically present as a solid prior to mixing with the polymer melt.

By-products of this reaction are mono-, di-, and/or trisodium citrate, in combination with other sodium salts, which will still be present within the foamed polymer. These residues are typically present at around 50 wt.% of the initial foaming agent formulation which is equivalent to <1 wt.% of the total foamed polymer in most cases [RAPRA, 2004].

Contributing activity/technique for the environment:

- Use in polymers and plastics products (ERC6b)

Contributing activity/technique for the workers:

- Use in polymers and plastics products (PROC 3; PROC 5; PROC 8a; PROC 8b)

Product Category used:

- PC 32: Polymer preparations and compounds

Sector of end use:

- SU 11: Manufacture of rubber products;
- SU 12: Manufacture of plastics products, including compounding and conversion

Technical function of the substance: foamant.

Substance supplied to that use: as such; in a mixture.

Related assessment: use assessed in a joint CSR.

**3.6. Use in the textile industry**

Further description of the use:

Within the textile and leather finishing industries, citric acid and related salts may be used in a wide variety of applications. However, these uses may be summarized (albeit with some overlap) as being based on either acidity (and pH regulation) or the ability to complex metal ions. Examples of applications where these are important are:

- Acidification of flame-retardant treating baths
- Curing catalyst for treatments such as easy-care resins
- Sequestering of alkaline earth or transition metal ions to prevent interference in dyeing and other processes.

Potential exposure to humans and especially the environment is dependent on the intended function of the substance, as well as the substrates and processes used. Functional finishing agents and other chemically reactive substances are intended to be consumed during use; therefore the amount released is related to the efficiency of the process. On the other hand, non-reacting substances (e.g. processing aids) are not consumed and will ultimately be lost to air or waste water, depending on their function and physicochemical properties. In virtually all cases, it is expected that citric acid or citrate salts, as process aids, will be lost to waste water.

The following applications should be taken as representative rather than exhaustive examples of where and why citric acid or citrates may be used within the textile and leather finishing industries. Further details of these examples may be found in European Commission Reference Document on Best Available Techniques for the Textiles Industry [BREF, 2003].

Flame Retardants: Potassium salts of fluoro complexes of zirconium (potassium hexafluorozirconate) are typically used as flame retardants for wool and wool-blend fibres. Typical application conditions for carpet wool yarn are as follows:

- Rinse to remove unwanted salts / anions.
- Bath set up at 20 – 30ºC and pH 3: citric acid (4 % on weight of fabric) may be used.
- Addition of potassium hexafluorozirconate dissolved in hot water.
- Temperature raised at 1 – 2 K per minute to 60ºC and held at this temperature for 30 minutes

- Rinse in cold water for 10 - 20 minutes.

Durable Press Resins: Cellulosic fabrics such as cotton or its blends are often treated with a finish which prevents wrinkling and shrinkage during laundering and drying. These finishes are known by a variety of names: easy-care, wash-and-wear finishing, no-iron, wrinkle resistant etc. Recipes for resin-finishing liquors are in general aqueous solutions or dispersions which consist of a cross- linking resin, a catalyst, a wetting agent/emulsifier (mainly a non-ionic surfactant) plus a number of additives. Cross-linking resin systems are often based on urea-formaldehyde or melamine- formaldehyde. The most commonly used catalyst is magnesium chloride. In many cases liquid mixtures are used, which are based on magnesium chloride plus an organic acid such as citric acid. Catalyst is used at 10 – 30 % of the weight of the cross-linking resin, which is itself used in the range of 5% (for blends) up to 12% (for 100% cotton) on the weight of the fabric. A typical bath may contain: cross-linking resin, 50 g/l; catalyst ($MgCl_2$), 7 g/l; and acid, 0.5 g/l.

Pre-treatment and Dyeing: The presence of ions of alkaline earth metals (calcium and magnesium) and/or other metals (especially iron) may have negative effects on various wet processes not only in pre-treatment (e.g. catalytic destruction of hydrogen peroxide) but also in dyeing. Purified and softened water is used in textile finishing mills but often this is not enough and specific auxiliary formulations containing metal complexing agents need to be added to the baths. Typical sequestering agents which have been used are polyphosphates, phosphonates, and amino carboxylic acids (e.g., EDTA). The main concerns associated with the use of these substances arise from their N- and P-content, their often-low biodegradability/bioeliminability, and their ability to form stable complexes with metals (the very reason they are used in the first place!), which may lead to remobilisation of heavy metals in effluent or downstream sediments.

Hydroxy-carboxylic acids (e.g., gluconates, citrates) are convenient alternatives to the above named conventional sequestering agents. None of these substances contains N or P in their molecular structure. In addition, hydroxy-carboxylic acids are readily biodegradable.

A typical hydrogen peroxide-based bleaching formulation for cotton (or its blends) will use 0 – 20g sequestering agent per kg of textile being treated. For bleaching of wool, 5 – 30 g/kg may be used. For dyeing of cellulosic fabrics, 1 – 3 g/litre of sequestering agent may be used.

Contributing activity/technique for the environment:

- Use in the textile industry (ERC4)

Contributing activity/technique for the workers:

- Use in the textile industry (PROC 8a; PROC 8b; PROC 10; PROC 13; PROC 22)

Product Category used:

- PC 20: Products such as ph-regulators, flocculants, precipitants, neutralisation agents
- PC 23: Leather treatment products
- PC 24: Lubricants, greases, release products

Sector of end use:

- SU 5: Manufacture of textiles, leather, fur

Technical function of the substance: chelating agent; flame retardant; softener; curing agent.

Substance supplied to that use: in a mixture.

Related assessment: use assessed in a joint CSR.

**3.7. Use in paints and coatings**

Further description of the use:

The following application should be taken as representative rather than the sole example of where and why citric acid or citrates may be used within the coatings industry.

Anti-settling of Pigment: In the paint industry citric acid and citrate salts are used to retard the settling of titanium dioxide, the most common pigment used in paints and other coatings [APAC, 2009]. Shipping of titanium dioxide as an aqueous slurry has advantages in handling and storage space versus shipping as a fine solid. Although titanium dioxide particles will initially disperse in water, they separate rapidly and in a short time will form a hard-packed sediment which is virtually impossible to re-disperse. The presence of ions such as calcium or iron causes flocculation, which exacerbates the problem. In the early 1970s, it was discovered that addition of 0.04 – 0.4% citric acid or tartaric acid or their simple salts (sodium, potassium, ammonium) substantially retarded the settling and packing of titanium dioxide particles in aqueous dispersions [US 3,663,284].

At least a portion of the citric acid added to aid shipment of the pigment is likely to still be present during formulation of the paint. Indeed, it is possible that further additions are made to allow re- dispersion of pigment in the final paint formulation.

Contributing activity/technique for the environment:

- Use in paints and coatings (ERC5)

Contributing activity/technique for the workers:

- Use in paints and coatings (PROC 7; PROC 8a; PROC 8b; PROC 10; PROC 11; PROC 19; PROC 21; PROC 24)

Product Category used:

- PC 9a: Coatings and paints, thinners, paint removes
- PC 9b: Fillers, putties, plasters, modelling clay
- PC 9c: Finger paints
- PC 18: Ink and toners
- PC 34: Textile dyes, and impregnating products

Sector of end use:

- SU 17: General manufacturing, e.g. machinery, equipment, vehicles, other transport equipment;
- SU 18: Manufacture of furniture;
- SU 19: Building and construction work Technical function of the substance: antiredeposition agent

Substance supplied to that use: as such.

Related assessment: use assessed in a joint CSR.

**3.8. Use in water treatment**

Further description of the use:

Citric acid may be used as a complexing agent to decrease scale formation and inhibit corrosion of metal equipment and pipelines.

This includes, for example, cleaning of (steam) boilers or reheaters, removal of calcium and rust layers from steam blocks and hot water systems, removal of rust in cleaning bilges and desalination units aboard ships, removal of mill scale from welding operations in nuclear reactors. It may also be used as an additive in circulating cooling water systems. These systems typically use high substance concentration at low discharges and would usually have a waste water treatment plant (WWTP) in place.

Citric acid would generally be formulated in an additive package prior to use, and typically supplied in aqueous solution form with active ingredient content of 25 – 65%.

Contributing activity/technique for the environment:

- Use in water treatment (ERC4; ERC7)

Contributing activity/technique for the workers:

- Use in water treatment (PROC 1; PROC 2; PROC 3; PROC 4; PROC 7; PROC 8a; PROC 8b; PROC 9; PROC 10; PROC 13; PROC 18; PROC 20; PROC 25)

Product Category used:

- PC 4: Anti-freeze and de-icing products
- PC 7: Base metals and alloys
- PC 14: Metal surface treatment products
- PC 16: Heat transfer fluids
- PC 17: Hydraulic fluids
- PC 20: Products such as ph-regulators, flocculants, precipitants, neutralisation agents
- PC 25: Metal working fluids
- PC 31: Polishes and wax blends
- PC 35: Washing and cleaning products
- PC 37: Water treatment chemicals

Sector of end use: SU 14: Manufacture of basic metals, including alloys; SU 15: Manufacture of fabricated metal products, except machinery and equipment; SU 16: Manufacture of computer, electronic and optical products, electrical equipment; SU 17: General manufacturing, e.g. machinery, equipment, vehicles, other transport equipment

Technical function of the substance: antiredeposition agent; antiscaling agent; chelating agent; cleaning agent.

Substance supplied to that use: as such; in a mixture.

Related assessment: use assessed in a joint CSR.

**3.9. Use in the treatment of metal surfaces**

Further description of the use:

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Citric acid may be used as a complexing agent during metal surface treatment operations. This includes cleaning, brightening and passivation of fabricated stainless steel components, and other metal components, cleaning of circuit boards prior to soldering, and metal cleaning or

chemical polishing for the surface treatment of aluminium, copper and other metals. The following applications should be taken as representative rather than the sole example of where and why citric acid or citrates may be used in the treatment of metal surfaces. Some industries using citric acid include fasteners, medical devices, semi-conductors, automotive and aerospace.

Passivation: Citric acid may be used in stainless steel passivation to assist oxidation of the surface of the stainless steel and prevent later corrosion. After thorough cleaning, the stainless steel part

is immersed in a passivating acid bath. Any one of three approaches can be used: nitric acid passivation, nitric acid with sodium dichromate passivation and citric acid passivation. Which approach to use depends on the grade of stainless steel and prescribed acceptance criteria. When citric acid passivation is used, typical solutions range from 4 to 10% citric acid by weight.

Electroless plating: Plating describes the coating of surfaces with metals, either through an electrolysis or electroless plating processes. Electroless plating is also known as 'autocatalytic' plating; deposition of the metal starts on metal nuclei such as palladium and continues autocatalytically. Electroless plating is favoured over electrolysis for most component production (EA 2009).

There are usually three stages in the electroless plating process: de-smearing, activation and electroless copper plating. The plating solution has a copper content of 2 – 5 g/l, with sodium hydroxide (15 – 20 g/l), complexing agents (10 – 15 g/l) or tartrates (5 – 10 g/l) and reducing agents, such as formaldehyde (3 – 5 g/l). The process solution lifetime is limited by the buildup of reaction products and is proportional to the rate of throughput of components (EA 2009). Citrate may be used as a complexing agent.

Electroless plating involves the large-scale use of water in both providing the medium for the process itself and for the subsequent rinsing and washing of components. There is a degree of recycling of rinse water through use to top-up the plating tanks, but there is ultimately loss through carry-over on components. Spent fluids can only be topped up a limited number of times before the media needs replacing. Water-soluble waste is discharged in waste water for basic on-site treatment (settling and pH adjustment) before discharge to municipal treatment works, controlled by local discharge consent agreements (EA 2009).

Contributing activity/technique for the environment:

- Use in the treatment of metal surfaces (ERC4; ERC6b)

Contributing activity/technique for the workers:

- Use in the treatment of metal surfaces (PROC 2; PROC 3; PROC 4; PROC 7; PROC 8a; PROC 8b; PROC 9; PROC 10; PROC 13; PROC 17; PROC 18; PROC 23)

Product Category used:

- PC 7: Base metals and alloys
- PC 14: Metal surface treatment products
- PC 25: Metal working fluids
- PC 31: Polishes and wax blends

- PC 35: Washing and cleaning products

Sector of end use:

- SU 14: Manufacture of basic metals, including alloys
- SU 15: Manufacture of fabricated metal products, except machinery and equipment
- SU 16: Manufacture of computer, electronic and optical products, electrical equipment
- SU 17: General manufacturing, e.g. machinery, equipment, vehicles, other transport equipment

Technical function of the substance: antioxidant; brightener; chelating agent; cleaning agent; corrosion inhibitor; passivation agent.

Substance supplied to that use: as such; in a mixture.

Related assessment: use assessed in a joint CSR.

**3.10. Use in agricultural applications**

Further description of the use:

One common method for making fertilisers involves dissolving metal sulfates in water and citric acid followed by neutralization with ammonia. This process may be carried out in an industrial setting as part of the formulation of solid or liquid fertilisers/plant feeds. In this case, citric acid is an intermediate and it is the metal-citrate or ammonium citrate that must be considered for the professional or consumer use of fertilisers/plant feeds. Magnesium citrate may be used in this context. Alternatively, mixing of fertilisers may take place on farms. In this case, exposure may be to solid or liquid citric acid or metal-citrate.

Contributing activity/technique for the environment:

- Use in agricultural applications (ERC4)

Contributing activity/technique for the workers:

- Use in agricultural applications (PROC 3; PROC 5; PROC 8a; PROC 8b; PROC 10; PROC 11; PROC 14; PROC 15; PROC 19)

Product Category used:

- PC 8: Biocidal products (e.g. disinfectants, pest control)
- PC 12: Fertilisers
- PC 21: Laboratory chemicals

Sector of end use:

- SU 1: Agriculture, forestry and fishing

Technical function of the substance: antiredeposition agent; antiscaling agent; intermediate (precursor); pH regulating agent.

Substance supplied to that use: as such; in a mixture.

Related assessment: use assessed in a joint CSR.

## 4. USES BY PROFESSIONAL WORKERS

### 4.1. Detergent and cleaning products and other household products

Further description of the use:

Citric acid and its salts are used in a wide variety of household products, as well as cleaning and maintenance products for industrial and professional uses. The large number of household products includes, but is not limited to:

- Laundry products: These include detergent powders, detergent liquids, laundry pretreatment products and fabric softeners.
- Dish washing products: These are hand dishwashing liquids and machine dishwashing products (dishwashing powders/detergents and dishwashing liquids/rinse aids).
- All purpose cleaners: These are used in cleaning hard surfaces like windows, mirrors, wood, floors and tiled walls [RIVM, 2006]. The products can be liquid cleaners, spray cleaners or wet tissue application.
- Abrasive cleaners: These are used in remove soil which is firmly attached to the surface (e.g. lavatory pan, washbasins and kitchen sink/ working top) and can be powders, liquids or scouring pads [RIVM, 2006]
- Sanitary products: These are bathroom cleaners (sprays and liquids) and toilet cleaners.
- Floor, carpet and furniture products: These are products that provide a combined effect of cleaning and polishing.
- Metal polish: Consumer or professional use of, e.g., silver polishes, either ready-to-use or solid preparations which need to be dissolved in water.
- Water treatment/scale inhibition products for household appliances.
- Vehicle care products.

The main use or function of citric acid and its salts in detergents and cleaning products is as a complexing agent/ sequestering builders to remove water hardness minerals and 'build' the cleaning efficiency of the surfactant. They can also function as additives (e.g. in handwashing liquids [RIVM, 2006]) or acids (e.g., in bathroom/ toilet cleaning liquids or silver polish).

Technical applications of citric acid and its salts in various industries as a complex-forming agent, cleaning agent, softening agent, decalcifying agent, de-rusting agent, corrosive agent and synergist in antioxidant mixtures accounted for 20% of the total production volume (500,000 tons/annum) in Europe (including Eastern Europe and Israel ) in 1999 [HERA, 2005]. The total consumption of citric acid in household cleaning applications in the EEA (i.e., EU + Iceland, Switzerland and Norway) in 2002 was 103,000 tons [HERA, 2005].

Contributing activity/technique for the environment:

- Detergent and cleaning products and other household products (ERC8a; ERC8d; ERC9a; ERC9b)

Contributing activity/technique for the workers:

- Detergent and cleaning products and other household products (PROC 1; PROC 2; PROC 4; PROC 5; PROC 7; PROC 8a; PROC 8b; PROC 9; PROC 10; PROC 11; PROC 13; PROC 19)

Product Category used:

- PC 3: Air care products
- PC 28: Perfumes, fragrances
- PC 31: Polishes and wax blends
- PC 35: Washing and cleaning products
- PC 36: Water softeners
- PC 37: Water treatment chemicals

Sector of end use:

- SU 0: Other: Professional uses

Technical function of the substance: abrasive; antioxidant; antiredeposition agent; antiscaling agent; brightener; chelating agent; cleaning agent; softener.

Related assessment: use assessed in a joint CSR.

**4.2. Use in the oil industry**

**Further description of the use:**

Citric acid may be used in on- and off-shore mining operations as a complexing or scaleinhibiting agent to prevent build up of solids that could otherwise complicate extractions.

Oil producing well formations can become plugged with acid soluble minerals and restrict fluid flow and reduce oil production [Gewanter, Herman L. et al]. Production can be increased by forcing acid down the well formations to dissolve the minerals [Gewanter, Herman L. et al].

The acids readily dissolve the iron and iron containing compounds from the well casing and the formation [Gewanter, Herman L. et al]. However, water and carbonates will neutralise the acid in the formation, which allows for the re-precipitation of the iron to ferric hydroxide above a pH of 2.2. [Gewanter, Herman L. et al]. Certain chemicals must be added at this point to maintain it in a soluble state [Gewanter, Herman L. et al].

Control of the re-precipitation of iron and the pH, as the acid is spent, can be achieved by the sequestration by organic chelants and the reduction to soluble ferrous iron [Gewanter, Herman L. et al]. Citric acid is a useful organic chelant and is used for this purpose [Gewanter, Herman L. et al]. Other chelants may include gluconic acid, the tetrasodium salt of ethylenediaminetetraacetic acid (EDTA), and the trisodium salt of nitrilotriacetic acid (NTA) [Gewanter, Herman L. et al].

Contributing activity/technique for the environment:

- Use in the oil industry (ERC8d)

Contributing activity/technique for the workers:

- Use in the oil industry (PROC 3; PROC 4; PROC 5; PROC 8a; PROC 8b)

Product Category used:

- PC 20: Products such as ph-regulators, flocculants, precipitants, neutralisation agents

- PC 40: Extraction agents

Sector of end use:

- SU 2a: Mining (without offshore industries)
- SU 2b: Offshore industries

Technical function of the substance: antiscaling agent; chelating agent.

Related assessment: use assessed in a joint CSR.

**4.3. Use in paints and coatings**

Further description of the use:

The following application should be taken as representative rather than the sole example of where and why citric acid or citrates may be used within the coatings industry.

Anti-settling of Pigment: In the paint industry citric acid and citrate salts are used to retard the settling of titanium dioxide, the most common pigment used in paints and other coatings [APAC, 2009]. Shipping of titanium dioxide as an aqueous slurry has advantages in handling and storage space versus shipping as a fine solid. Although titanium dioxide particles will initially disperse in water, they separate rapidly and in a short time will form a hard-packed sediment which is virtually impossible to re-disperse. The presence of ions such as calcium or iron causes flocculation, which exacerbates the problem. In the early 1970s, it was discovered that addition of 0.04 – 0.4% citric acid or tartaric acid or their simple salts (sodium, potassium, ammonium) substantially retarded the settling and packing of titanium dioxide particles in aqueous dispersions [US 3,663,284].

At least a portion of the citric acid added to aid shipment of the pigment is likely to still be present during formulation of the paint. Indeed, it is possible that further additions are made to allow re- dispersion of pigment in the final paint formulation.

Contributing activity/technique for the environment:

- Use in paints and coatings (ERC8c; ERC8f)

Contributing activity/technique for the workers:

- Use in paints and coatings (PROC 7; PROC 8a; PROC 8b; PROC 10; PROC 11; PROC 19; PROC 21; PROC 24)

Product Category used:

- PC 9a: Coatings and paints, thinners, paint removes
- PC 9b: Fillers, putties, plasters, modelling clay
- PC 18: Ink and toners
- PC 34: Textile dyes, and impregnating products

Sector of end use:

- SU 17: General manufacturing, e.g. machinery, equipment, vehicles, other transport equipment
- SU 18: Manufacture of furniture
- SU 19: Building and construction work

Technical function of the substance: antiredeposition agent.

Related assessment: use assessed in a joint CSR.

**4.4. Use in personal care products**

Further description of the use:

Citric acid and its salts are used in a wide range of personal care products, including:

- Shampoos and conditioners
- Astringent lotions
- Bubble baths
- Creams and lotions
- Facial cleaners
- Feminine hygiene products
- Permanent wave neutraliser
- Propellants for aerosol-type dispensers
- Toothpastes
- Mouth rinses
- Body wash/cleanser
- Hair colour and bleaching
- Moisturisers
- Hand soaps
- Nail polish
- Anti-aging products

Contributing activity/technique for the environment:

- Use in personal care products (ERC8a)

Contributing activity/technique for the workers:

- Use in personal care products (PROC 10; PROC 11; PROC 19)

Product Category used:

- PC 2: Adsorbents
- PC 39: Cosmetics, personal care products

Sector of end use:

- SU 20: Health services

Technical function of the substance: chelating agent; cleaning agent; foamant; softener; stabilising agent.

Related assessment: use assessed in a joint CSR.

**4.5. Use in photography products**

Further description of the use:

Citric acid is one of a range of complexing agents used in photography to control the effects of calcium and magnesium hardness, and to keep iron soluble in solution as part of redox processes. Due to the rapid growth of digital photography, use of chemicals in film processing is now limited almost entirely to a small number of professional providers. The chemicals used are collected by photochemical companies in order to recover silver and disposal to drain does not take place.

Contributing activity/technique for the environment:

- Use in photography products (ERC8a)

Contributing activity/technique for the workers:

- Use in photography products (PROC 5; PROC 13)

Product Category used:

- PC 30: Photo-chemicals

Sector of end use:

- SU 20: Health services

Technical function of the substance: chelating agent.

Related assessment: use assessed in a joint CSR.

**4.6. Use in agricultural applications**

Further description of the use:

One common method for making fertilisers involves dissolving metal sulfates in water and citric acid followed by neutralization with ammonia. This process may be carried out in an industrial setting as part of the formulation of solid or liquid fertilisers/plant feeds. In this case, citric acid is an intermediate and it is the metal-citrate or ammonium citrate that must be considered for the professional or consumer use of fertilisers/plant feeds. Magnesium citrate may be used in this context. Alternatively, mixing of fertilisers may take place on farms. In this case, exposure may be to solid or liquid citric acid or metal-citrate.

Contributing activity/technique for the environment:

- Use in agricultural applications (ERC8b; ERC8d)

Contributing activity/technique for the workers:

- Use in agricultural applications (PROC 3; PROC 5; PROC 8a; PROC 8b; PROC 10; PROC 11; PROC 14; PROC 15; PROC 19)

Product Category used:

- PC 8: Biocidal products (e.g. disinfectants, pest control)

- PC 12: Fertilisers
- PC 21: Laboratory chemicals

Sector of end use:

- SU 1: Agriculture, forestry and fishing

Technical function of the substance: antiredeposition agent; antiscaling agent; intermediate (precursor); pH regulating agent.

Related assessment: use assessed in a joint CSR.

## 5. CONSUMER USES

### 5.1. Detergent and cleaning products and other household products

Further description of the use:

Citric acid and its salts are used in a wide variety of household products, as well as cleaning and maintenance products for industrial and professional uses. The large number of household products includes, but is not limited to:

- Laundry products: These include detergent powders, detergent liquids, laundry pretreatment products and fabric softeners.
- Dish washing products: These are hand dishwashing liquids and machine dishwashing products (dishwashing powders/detergents and dishwashing liquids/rinse aids).
- All purpose cleaners: These are used in cleaning hard surfaces like windows, mirrors, wood, floors and tiled walls [RIVM, 2006]. The products can be liquid cleaners, spray cleaners or wet tissue application.
- Abrasive cleaners: These are used in remove soil which is firmly attached to the surface (e.g. lavatory pan, washbasins and kitchen sink/ working top) and can be powders, liquids or scouring pads [RIVM, 2006]
- Sanitary products: These are bathroom cleaners (sprays and liquids) and toilet cleaners.
- Floor, carpet and furniture products: These are products that provide a combined effect of cleaning and polishing.
- Metal polish: Consumer or professional use of, e.g., silver polishes, either ready-to-use or solid preparations which need to be dissolved in water.
- Water treatment/scale inhibition products for household appliances.
- Vehicle care products.

The main use or function of citric acid and its salts in detergents and cleaning products is as a complexing agent/ sequestering builders to remove water hardness minerals and ‘build’ the cleaning efficiency of the surfactant. They can also function as additives (e.g. in handwashing liquids [RIVM, 2006]) or acids (e.g., in bathroom/ toilet cleaning liquids or silver polish).

Technical applications of citric acid and its salts in various industries as a complex-forming agent, cleaning agent, softening agent, decalcifying agent, de-rusting agent, corrosive agent and synergist in antioxidant mixtures accounted

for 20% of the total production volume (500,000 tons/annum) in Europe (including Eastern Europe and Israel ) in 1999 [HERA, 2005]. The total consumption of citric acid in household cleaning applications in the EEA (i.e., EU + Iceland, Switzerland and Norway) in 2002 was 103,000 tons [HERA, 2005].

Contributing activity/technique for the environment:

- Detergent and cleaning products and other household products (ERC8a; ERC8d; ERC9a; ERC9b)

Contributing activity/technique for consumers:

- Detergent and cleaning products and other household products (PC 3; PC 28; PC 31; PC 35; PC 36; PC 37)

Technical function of the substance: abrasive; antioxidant; antiredeposition agent; antiscaling agent; brightener; chelating agent; cleaning agent; softener.

Related assessment: use assessed in a joint CSR.

**5.2. Use in paints and coatings**

Further description of the use:

The following application should be taken as representative rather than the sole example of where and why citric acid or citrates may be used within the coatings industry.

Anti-settling of Pigment: In the paint industry citric acid and citrate salts are used to retard the settling of titanium dioxide, the most common pigment used in paints and other coatings [APAC, 2009]. Shipping of titanium dioxide as an aqueous slurry has advantages in handling and storage space versus shipping as a fine solid. Although titanium dioxide particles will initially disperse in water, they separate rapidly and in a short time will form a hard-packed sediment which is virtually impossible to re-disperse. The presence of ions such as calcium or iron causes flocculation, which exacerbates the problem. In the early 1970s, it was discovered that addition of 0.04 – 0.4% citric acid or tartaric acid or their simple salts (sodium, potassium, ammonium) substantially retarded the settling and packing of titanium dioxide particles in aqueous dispersions [US 3,663,284].

At least a portion of the citric acid added to aid shipment of the pigment is likely to still be present during formulation of the paint. Indeed, it is possible that further additions are made to allow re- dispersion of pigment in the final paint formulation.

Contributing activity/technique for the environment:

- Use in paints and coatings (ERC8c; ERC8f)

Contributing activity/technique for consumers:

- Use in paints and coatings (PC 9a; PC 9b; PC 9c; PC 18; PC 34)

Technical function of the substance: antiredeposition agent.

Related assessment: use assessed in a joint CSR.

**5.3. Use in personal care products**

Further description of the use:

Citric acid and its salts are used in a wide range of personal care products, including:

- Shampoos and conditioners
- Astringent lotions
- Bubble baths
- Creams and lotions
- Facial cleaners
- Feminine hygiene products
- Permanent wave neutraliser
- Propellants for aerosol-type dispensers
- Toothpastes
- Mouth rinses
- Body wash/cleanser
- Hair colour and bleaching
- Moisturisers
- Hand soaps
- Nail polish
- Anti-aging products

Contributing activity/technique for the environment:

- Use in personal care products (ERC8a)

Contributing activity/technique for consumers:

- Use in personal care products (PC 2; PC 39)

Technical function of the substance: chelating agent; cleaning agent; foamant; softener; stabilising agent.

Related assessment: use assessed in a joint CSR.

**5.4. Use in photography products**

Further description of the use:

Citric acid is one of a range of complexing agents used in photography to control the effects of calcium and magnesium hardness, and to keep iron soluble in solution as part of redox processes. Due to the rapid growth of digital photography, use of chemicals in film processing is now limited almost entirely to a small number of professional providers. The chemicals used are collected by photochemical companies in order to recover silver and disposal to drain does not take place.

Contributing activity/technique for the environment:

- Use in photography products (ERC8a)

Contributing activity/technique for consumers:

- Use in photography products (PC 30)

Technical function of the substance: chelating agent.

Related assessment: use assessed in a joint CSR.

**5.5. Use in agricultural applications**

Further description of the use:

One common method for making fertilisers involves dissolving metal sulfates in water and citric acid followed by neutralization with ammonia. This process may be carried out in an industrial setting as part of the formulation of solid or liquid fertilisers/plant feeds. In this case, citric acid is an intermediate and it is the metal-citrate or ammonium citrate that must be considered for the professional or consumer use of fertilisers/plant feeds. Magnesium citrate may be used in this context. Alternatively, mixing of fertilisers may take place on farms. In this case, exposure may be to solid or liquid citric acid or metal-citrate.

Contributing activity/technique for the environment:

- Use in agricultural applications (ERC8b; ERC8d)

Contributing activity/technique for consumers:

- Use in agricultural applications (PC 8; PC 12; PC 21)

Technical function of the substance: antiredeposition agent; antiscaling agent; intermediate (precursor); pH regulating agent

Related assessment: use assessed in a joint CSR.

## 6. ARTICLE SERVICE LIFE

**6.1. Personal care products**

Further description of the use:

Citric acid and its salts are used in a wide range of personal care products, including:

- Shampoos and conditioners
- Astringent lotions
- Bubble baths
- Creams and lotions
- Facial cleaners
- Feminine hygiene products
- Permanent wave neutraliser

- Propellants for aerosol-type dispensers
- Toothpastes
- Mouth rinses
- Body wash/cleanser
- Hair colour and bleaching
- Moisturisers
- Hand soaps
- Nail polish
- Anti-aging products

Article used by: workers; consumers Substance intended to be released from article:

Article category related to subsequent service life (AC): AC 8: Paper articles Contributing activity/technique for the environment:

- Personal care products (ERC11a)

Contributing activity/technique for consumers:

- Personal care products (AC 8)

Contributing activity/technique for the workers:

- Personal care products (PROC 10; PROC 11; PROC 19)

Technical function of the substance: chelating agent; cleaning agent; foamant; softener; stabilising agent.

Related assessment: use assessed in a joint CSR.

**6.2. Use in paints and coatings**

Further description of the use:

The following application should be taken as representative rather than the sole example of where and why citric acid or citrates may be used within the coatings industry.

Anti-settling of Pigment: In the paint industry citric acid and citrate salts are used to retard the settling of titanium dioxide, the most common pigment used in paints and other coatings [APAC, 2009]. Shipping of titanium dioxide as an aqueous slurry has advantages in handling and storage space versus shipping as a fine solid. Although titanium dioxide particles will initially disperse in water, they separate rapidly and in a short time will form a hard-packed sediment which is virtually impossible to re-disperse. The presence of ions such as calcium or iron causes flocculation, which exacerbates the problem. In the early 1970s, it was discovered that addition of 0.04 – 0.4% citric acid or tartaric acid or their simple salts (sodium, potassium, ammonium) substantially retarded the settling and packing of titanium dioxide particles in aqueous dispersions [US 3,663,284].

# Annex. Exposure Scenarios
# Citric Acid

At least a portion of the citric acid added to aid shipment of the pigment is likely to still be present during formulation of the paint. Indeed, it is possible that further additions are made to allow re- dispersion of pigment in the final paint formulation.

Article used by: workers; consumers

Substance intended to be released from article:

Article category related to subsequent service life (AC):

- AC 4: Stone, plaster, cement, glass and ceramic articles
- AC 11: Wood articles

Contributing activity/technique for the environment:

- Use in paints and coatings (ERC10a; ERC10b; ERC11a; ERC11b)

Contributing activity/technique for consumers:

- Use in paints and coatings (AC 4; AC 11)

Contributing activity/technique for the workers:

Technical function of the substance: antiredeposition agent.

Related assessment: use assessed in a joint CSR.

**Note**: Chemical Safety Report based on leader information. Full Chemical Safety Report prepared by competent person (lead registrant).