

Peroxo Compounds, Inorganic

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1. Introduction

Peroxo compounds include hydrogen peroxide (\rightarrow Hydrogen Peroxide) and substances derived from hydrogen peroxide by substitution of one or both hydrogen atoms by a metal or a nonmetal such as sulfur, boron, nitrogen, or phosphorous. Peroxides in a wider sense also include the hyperoxides (MO_2), H_2O_2 addition compounds (e.g., sodium carbonate peroxohydrate), and the inorganic ozonides (M^+O_3^-). In the IUPAC nomenclature, the prefix peroxo is used for inorganic compounds, and peroxy for organic compounds.

A very large number of peroxo compounds have been described in the literature [1–5]. This article gives an overview on the properties and industrial applications of the most important peroxo compounds and products of commercial importance.

Due to the low strength of the $-\text{O}-\text{O}-$ bonding (209 kJ/mol), all peroxo compounds exhibit powerful oxidizing properties. Inorganic peroxo compounds are therefore employed as oxidizing and bleaching agents in the detergents, textile, electronics, and chemical industries.

1.1. History

The first peroxo compounds discovered in the early 1800s by GAY-LUSSAC and THENARD were the peroxides of barium, sodium, and potassium. Hydrogen peroxide was isolated several years later in 1818 by THENARD. Due to the advantages in stability and handling, the solid peroxides were of greater practical use than hydrogen peroxide solutions. Sodium peroxide gained industrial importance mainly as a bleaching agent in the textile industry and was first produced on a commercial scale by the Castner process in 1899. Sodium peroxide lost its importance when hydrogen peroxide could be more cost-effectively manufactured by the anthraquinone process.

Today the most important industrial peroxo compound is sodium carbonate peroxohydrate. Although discovered in 1899 by TANATAR it only gained commercial importance in the 1990s due to the ecologically driven shift from sodium perborate to sodium carbonate peroxohydrate, especially in Europe. It has nowadays become the preferred bleaching agent in powder laundry and automatic dishwashing detergents since products with good shelf-life properties have become available through new economically viable coating technologies. Sodium peroxoborates, also discovered by TANATAR, in 1898, have been produced on a commercial scale since 1907 and still remain the preferred bleaching agents in powder laundry and automatic dishwashing detergents for climatically challenging regions such as the Middle East, northern Africa, and South and Middle America.

Other industrially important inorganic peroxo compounds are the sodium, potassium, and ammonium salts of peroxodisulfuric acid ($\text{H}_2\text{S}_2\text{O}_8$), the triple salt of potassium peroxomonosulfate ($2 \text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), and calcium peroxide (CaO_2).

Of the other hydrogen peroxide addition compounds, only urea peroxide is produced on an industrial scale of several hundred tonnes; it has limited applications in pharmaceutical products.

1.2. Classification of Peroxo Compounds

WANNAGAT [6] proposed that the peroxo compounds should be classified according to their

chemical bonding, i.e., whether the bond between the peroxo group and the substituent(s) is heteropolar, covalent, or dative. However, a precise distinction is often impossible, either because of continuous gradation between the bonding types or because the structure has not yet been fully elucidated.

Peroxo Compounds with Heteropolar Bonds Compounds of this type crystallize in an ionic lattice and contain the colorless, diamagnetic O_2^{2-} anion. The distance between the oxygen atoms is 149 pm. Typical examples of this class are the alkali and alkaline earth metal peroxides M_2O_2 or $\text{M}^{\text{II}}\text{O}_2$.

Peroxo Compounds with Covalent Bonds The typical example for this group is hydrogen peroxide itself. Whereas the paramagnetic oxygen molecule has a multiple bond (bond length 121 pm), the O–O distance for these compounds is 147 pm, indicating a covalent single bond. The two hydrogen atoms are linked to the O_2 moiety to form a nonplanar structure. Elements of Groups 13–16 of the periodic table, such as boron, carbon, silicon, phosphorus, and sulfur, also form covalent or mainly covalent bonds with the peroxo group. Either one or both hydrogen atoms of hydrogen peroxide can be substituted. Industrially important examples of these compounds are peroxoborates, most organic peroxy compounds (\rightarrow Peroxy Compounds, Organic), the silyl peroxides, and the peroxomono- and peroxodiphosphates and -sulfates. Peroxo compounds with covalent bonds to the O_2 group are colorless.

Peroxo Compounds with Dative Bonds These are metal complexes with peroxo ligands and are formed by polyvalent transition metal cations such as Ti, Cr, Mo, W, and U. They are sometimes colored. An unambiguous assignment is, however, difficult in the case of these compounds. They can sometimes be regarded as peroxohydrates (see below) or as peroxyacids with covalent bonds. They have no industrial importance.

Peroxyhydrates With many substances hydrogen peroxide forms crystalline adducts in which it behaves like water of crystallization, which may also be present in the crystal structure.

The peroxohydrates are also regarded as peroxo compounds.

Hyperoxides are classified as peroxo compounds only in a broad sense. The paramagnetic O_2^- anion (O–O distance: 128 pm, measured in KO_2) is a derivative of the very unstable HO_2 radical. The only known pure hyperoxides are those of the alkali metals, with the exception of lithium.

Inorganic Ozonides of the type $\text{M}^{\text{I}}\text{O}_3$ are also only classified as peroxo compounds in a broad sense. The name ozonides was proposed by REMY [7]. The O_3^- ion is paramagnetic, as is the O_2^- ion, and has a bent structure, with a bond angle of 100° and an O–O distance of 119 pm.

1.3. Properties

Oxygen is present in the peroxo group in the comparatively unstable oxidation state -1 . Hydrogen peroxide can behave as an oxidizing or reducing agent, depending on the coreactant, with the oxygen gaining or losing electrons to attain the more stable oxidation state -2 or 0 . Most inorganic peroxides, however, act predominantly as oxidizing agents.

Another typical property of many peroxo compounds is their ready decomposition to form radicals. The first step is homolytic cleavage of the O–O bond, which can be initiated either thermally or catalytically (e.g., by metal ions). The industrial importance of many organic and inorganic peroxides as polymerization accelerators is based on this behavior.

Another typical reaction is exothermic redox disproportionation. This type of reaction is the cause of the loss of active oxygen on prolonged storage or heating. The decomposition can be suppressed or considerably reduced by adding small quantities of stabilizers such as magnesium sulfate or sodium silicate. Many commercial peroxo compounds stabilized in this way have extremely good storage stability at room temperature. All aqueous solutions of peroxo compounds hydrolyze forming hydrogen peroxide.

The alkali metal hyperoxides are very powerful oxidizing agents and react vigorously with water to form hydroxides with liberation of oxygen. The alkali metal ozonides are unstable

and readily decompose to form hyperoxides and oxygen; they also form alkali metal hydroxides and oxygen with water.

1.4. Analysis

The quantitative determination of peroxidic oxygen in peroxo compounds is usually carried out by hydrolysis in aqueous solution to form H_2O_2 , followed by titration with permanganate, cerium(IV) sulfate or potassium iodide/thiosulfate, giving the so-called active oxygen content in weight percent. This terminology is historic and is based on the incorrect assumption that one of the oxygen atoms is initially split off from the peroxo group as atomic oxygen. Thus, in 1 mol H_2O_2 (34 g) the active oxygen content is 16 g or 47.06 wt %.

2. Peroxides, Hyperoxides, and Ozonides of the Alkali and Alkaline Earth Metals

2.1. Peroxides

The alkali and alkaline earth metals form peroxides with the general formulae $\text{M}_2^{\text{I}}\text{O}_2$ and $\text{M}^{\text{II}}\text{O}_2$, respectively, which crystallize with an ionic lattice and contain the diamagnetic O_2^{2-} anion. In the case of lithium and the elements of Group 2 of the periodic table, the preparation can be carried out in aqueous solution from the hydroxides and hydrogen peroxide, but the alkali metal peroxides and also barium peroxide are better produced by oxidation of the metal or metal oxide. All these compounds are colorless or light yellow, the color being caused by small amounts of the hyperoxides. The alkali and alkaline earth metal peroxides are powerful oxidizing agents that usually have good stability in the pure state if stored with exclusion of moisture. If they come into contact with organic materials or other reductants, there is danger of spontaneous ignition or even explosion.

Most of all these peroxides form many hydrates and peroxohydrates. They dissolve in water exothermically, forming hydrogen peroxide and the hydroxide of the metal. The alkali metal peroxides form compounds with a number

of penta- and hexavalent heavy metal, oxides, e.g., of vanadium, molybdenum, tungsten and uranium, with the general formulas $2 M_2^I O_2 \cdot M_2^V O_5$ and $M_2^I O_2 \cdot M^VI O_3$ [8].

2.1.1. Sodium Peroxide

Sodium peroxide was produced on a large scale for many years, and was an important raw material in the synthesis of sodium peroxoborates and sodium carbonate peroxohydrate. In the early 1980s, most of the large-scale plants ceased production because the more cost-effective hydrogen peroxide produced by the autoxidation process replaced sodium peroxide in most industrial applications. Today sodium peroxide is used only in small quantities for specialty applications, e.g., as a fusion agent in chemical analysis.

Properties Sodium peroxide, [1313-60-6], Na_2O_2 , M_r 78.0, ρ 2.6 g/cm³, is a yellowish white powder with a theoretical active oxygen content of 20.5 wt %. It melts at ca. 660 °C and decomposes above 300 °C with liberation of oxygen. The oxygen dissociation pressure is 101.3 kPa (1 atm) [9]. Sodium peroxide is hygroscopic, but in the absence of moisture it exhibits good shelf life.

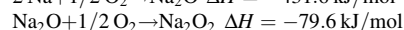
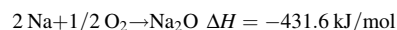
Sodium peroxide is a powerful oxidizing agent. In contact with organic materials or other reducing agents, spontaneous ignition and even explosion can occur. Sodium peroxide dissolves exothermically in water to form sodium hydroxide and hydrogen peroxide. Sodium peroxide

reacts with hydrogen gas yielding sodium hydroxide [10].

Sodium peroxide forms several peroxohydrates and hydrates, namely: $Na_2O_2 \cdot 2 H_2O_2$, $Na_2O_2 \cdot 2 H_2O_2 \cdot 4 H_2O$, $Na_2O_2 \cdot 2 H_2O$, and $Na_2O_2 \cdot 8 H_2O$ [8].

In Europe sodium peroxide is manufactured by Meteaux Speciaux in France.

Production GAY-LUSSAC and THENARD first prepared sodium peroxide in 1811 by the combustion of sodium metal. This method formed the basis for the large-scale production of this compound. The oxidation to sodium peroxide takes place with intermediate formation of sodium oxide:



The first industrial process for the manufacture of sodium peroxide was the block process, developed by CASTNER in 1891 and operated by Degussa in Rheinfelden since 1899, and later developed in several stages to give the classical continuous rotary furnace process [11]. Another continuous process which has long been in use is the U.S. Industrial Chemicals Process (USI Process) [12].

Rotary Furnace Process (Fig. 1). The sodium is oxidized in two stages. In the first stage, molten sodium is continuously fed countercurrently with an excess of dry air into a rotary furnace (the combustion furnace, b), which con-

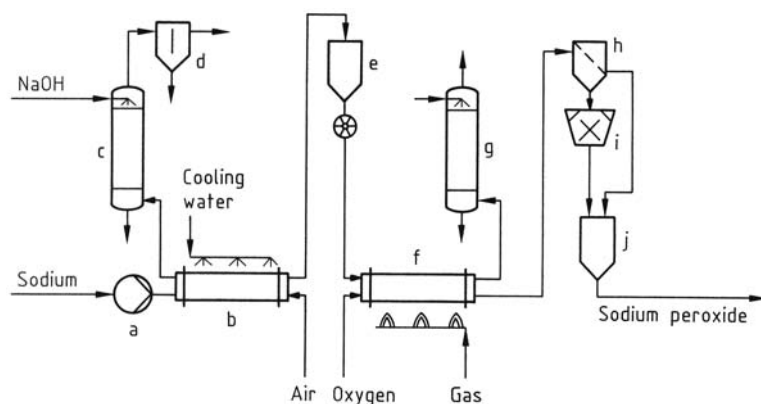


Figure 1. Production of sodium peroxide by the rotary furnace process a) Pump; b) Combustion furnace; c) Scrubber; d) Separator; e) Bunker; f) Finishing reactor; g) Scrubber; h) Sieve; i) Mill; j) Bunker

tains previously formed sodium oxide in powder form. The furnace rotates at ca. 2 rpm and is cooled externally with water because of the exothermic reaction. The reactor temperature is 600–700 °C near the entry point of the sodium, falling to 150–200 °C at the discharge end. The sodium oxide leaving the rotary furnace contains a few percent sodium peroxide and a maximum of 1 % of sodium metal. After intermediate storage in a bunker (e), it is fed by a screw conveyor or traveling containers via a lock to the next stage for further oxidation in a rotary reactor lined with sheet nickel (f). Because of the low exothermicity of the peroxide formation, this reactor is located in a brick-lined muffle furnace heated by gas or oil; it rotates at about the same speed as the combustion furnace. The oxidizing agent is oxygen from an air separation plant, which is introduced in co-current flow with the sodium oxide. It is important to maintain the reaction temperature at the optimum value of 350–400 °C, otherwise the product can stick on the reactor wall and lose its free-flowing properties. After leaving the reactor, the sodium peroxide is cooled and then screened into the various particle size fractions. The product consists of small pale yellow spheres with a sodium peroxide content of ca. 99 %. The off-gases from the two furnaces are purified by scrubbers (c, g) and a separator (d).

USI Process [12]. In the USI process, like the rotary furnace process, sodium oxide is produced in the first stage by reaction of sodium metal with recycled off-spec sodium peroxide. The reactants are mixed at ca. 120 °C in a nitrogen atmosphere and then heated in a reactor at > 250 °C. Since excess sodium peroxide is used, a mixture of sodium peroxide and sodium oxide is obtained. This is oxidized by air in a heated rotary furnace to form the peroxide. The product is classified, and the fine and coarse material recirculated to the first stage. Since the process is operated exclusively with air as the oxidizing agent, 80–90 % of the peroxide formed must be recycled.

2.1.2. Other Peroxides

Lithium Peroxide [12031-80-0], Li_2O_2 , M_r 45.9, ρ 2.36 g/cm³, has good thermal stability and, unlike Na_2O_2 , is not hygroscopic. The theoretical active oxygen content is 34.8 wt %,

which is the highest of all metal peroxides. It has not attained industrial importance due to the comparatively high cost of lithium and its compounds and high manufacturing costs, among other reasons.

Lithium peroxide can be produced by the reaction of dilute aqueous solutions of lithium hydroxide with 30 wt % hydrogen peroxide to form lithium peroxide monoperoxohydrate trihydrate ($\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 3 \text{H}_2\text{O}$), which is then dehydrated over phosphorus pentoxide or under vacuum [13]. Other methods include the reaction of lithium alkoxides in alcoholic solution with concentrated hydrogen peroxide [14], and the treatment of solid lithium oxide hydrate with concentrated hydrogen peroxide, followed by washing the precipitate with methanol and drying in a conveying dryer [15]. Another process has been proposed in which hydrogen peroxide and saturated lithium hydroxide solution are sprayed together into a spray dryer [15].

Calcium and Strontium Peroxides Calcium peroxide [1305-79-9], CaO_2 , M_r 72.1, ρ 2.92 g/cm³, theoretical active oxygen content 22.2 wt %, and strontium peroxide [1314-18-7], SrO_2 , M_r 119.6, ρ 4.7 g/cm³, theoretical active oxygen content 13.4 wt %, are produced by precipitation of the octahydrate from an aqueous solution of a salt or hydroxide, followed by dehydration at temperatures above 100 °C [16]. The thermal stability of strontium peroxide (decomp. ca. 410 °C) is marginally higher than that of calcium peroxide (decomp. ca. 375 °C). The active oxygen content of the commercial products is only 60–90 % of the theoretical value. Calcium peroxide is sold under the trade name PermeOx by FMC. Calcium peroxide is also manufactured by Solvay.

Calcium peroxide is used as oxygen source in the leaching of gold and silver ores with cyanide to improve precious metal recovery and leaching kinetics [17]. A relatively new application for CaO_2 is as a peroxide source in toothpaste [18] and dental chewing gum products. Calcium peroxide is also used in limited quantities as a hardening accelerator for sulfide rubber, as dough conditioner in the baking industry, and as a nontoxic disinfectant for seed and grain [19–21].

Strontium peroxide is used in pyrotechnics and tracer bullet formulations.

Barium Peroxide [1304-29-6], BaO_2 , M_r 169.4, ρ 5.4 g/cm³, theoretical active oxygen content 9.4 wt %, was the earliest known peroxo compound. It was used until the mid-1900s as the starting material for the production of hydrogen peroxide by the Thenard reaction [22].

Barium peroxide is the only peroxide of the Group 2 metals that can be prepared at atmospheric pressure by air oxidation of the oxide. Air is passed over finely spread barium oxide at 500–550 °C. On further heating in air to ca. 700 °C, oxygen is liberated [23]. On the industrial scale, barium peroxide is produced in a rotary furnace in the presence of a small quantity of steam to accelerate the reaction. Today barium peroxide has only limited application in the manufacture of fireworks.

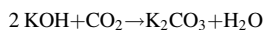
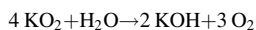
Magnesium and Zinc Peroxides. Magnesium peroxide [14452-57-4], MgO_2 , M_r 56.3, and zinc peroxide [1314-22-3], ZnO_2 , M_r 97.3, are manufactured in the same way as calcium and strontium peroxides [24]. However, well-defined compounds are not obtained, but mixtures of peroxohydrates and hydroxides with a peroxide content between 25 and 50 wt %. Zinc peroxide is used in dusting powders, as a deodorant, and in pharmacology for the treatment of infections and skin lesions. Recently, magnesium peroxide has been promoted as a oxygen-release compound for soil remediation [25]. Producers of magnesium peroxide are Solvay, Regenesis and FMC.

2.2. Hyperoxides

Hyperoxides, which are derived from the unstable HO_2 radical, have been described for some of the highly electropositive alkali and alkaline earth metals [26], [27]. Only potassium hyperoxide has a limited commercial importance.

Potassium hyperoxide [12030-88-5], KO_2 , M_r 71.1, ρ 2.14 g/cm³, is a paramagnetic yellow solid for which melting points between 380 °C and 440 °C have been reported [30]. The physical properties of KO_2 are summarized in [28], [29]. It is used as an oxygen generator and carbon dioxide absorber in breathing apparatus and gas masks. This application is based on the ability of potassium hyperoxide to simultaneously give off oxygen and absorb carbon dioxide in the

presence of water vapor. The following reactions take place above 20 °C:



Potassium hyperoxide can be prepared from potassium hydroxide and concentrated hydrogen peroxide, which are allowed to react under cooling at reduced pressure to give potassium peroxide diperoxohydrate $\text{K}_2\text{O}_2 \cdot 2 \text{H}_2\text{O}_2$ [31], [32]. It decomposes at elevated temperature to form KO_2 (dehydration in a vacuum or spray drying). Another industrial process [33] uses potassium metal as the starting material (Fig. 2). Molten potassium is sprayed into a closed reactor (c) where it reacts with a large excess of preheated air at ca. 75 °C. The reaction is highly exothermic, and the temperature in the reactor reaches ca. 300 °C. The powdered product is removed by a screw conveyor and is then granulated.

KO_2 is manufactured by Mine Safety Appliance Company (USA).

2.3. Ozonides

Ozonides of the alkali metals with the general formula M^1O_3 , can, with the exception of lithium ozonide, be prepared by the reaction of ozone-oxygen mixtures with the solid hydroxide, or

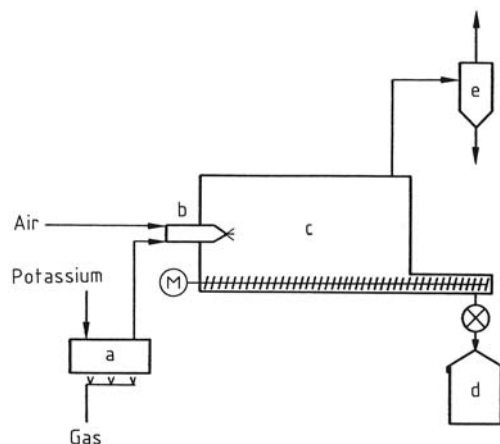


Figure 2. Production of potassium peroxide a) Molten salt vessel; b) Spray nozzle; c) Reactor; d) Receiving vessel; e) Cyclone

preferably the hyperoxide, of the metal. These compounds are dark in color and paramagnetic. They are not very stable; the stability increases with increasing atomic mass of the metal. They decompose readily into the hyperoxide and oxygen [2]. Ozonides have no industrial importance.

3. Peroxoborates

3.1. Sodium Peroxoborates

3.1.1. Properties

Sodium peroxoborate exists as the hexahydrate, the tetrahydrate, the trihydrate, the water-of-crystallization-free substance, and the anhydrous substance. Anhydrous sodium perborate (trade name: Oxoborate) is not a peroxoborate compound. The naming of the sodium peroxoborates has long been confused. Table 1 lists the trivial names and systematic IUPAC nomenclature, CAS numbers, formulas, and molecular structures of the sodium peroxoborates and anhydrous sodium perborate. Most commonly used in the

detergent industry are the names sodium perborate tetrahydrate and sodium perborate monohydrate. Sodium perborate trihydrate has no industrial importance.

Sodium perborate tetrahydrate was first prepared in 1898 by TANATAR and by MELIKOFF and PISSARJEWSKI by the action of hydrogen peroxide on a solution of borax and sodium hydroxide [34]. The long-running controversy as to whether this is a peroxo salt or an addition compound of H_2O_2 was ultimately resolved by HANSSON in 1961 by a single-crystal X-ray structure analysis [35].

The molecular structure (Fig. 3) consists of dimeric $[(\text{HO})_2\text{BOO}]^-$ units, which form centrosymmetric cyclic anions with two peroxo bridges. The sodium cations are coordinated by the water of crystallization and by certain hydroxide groups of the six-membered ring. The anions and cations form a polymeric structure.

An X-ray structural analysis of sodium perborate trihydrate [36], together with physicochemical investigations of the monohydrate, has shown that these compounds also contain the above-mentioned six-membered ring structure [37].

Table 1. The sodium peroxoborates

Common name	CAS registry no.	Historical formula	IUPAC name and constitutional formula
Sodium peroxoborate hexahydrate	[10486-00-7]	$\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3 \text{H}_2\text{O}$	disodium di- μ -peroxo-bis(dihydroxoborate) hexahydrate
Sodium perborate tetrahydrate	[13517-20-9]	$\text{NaBO}_3 \cdot 4 \text{H}_2\text{O}$	$2 [\text{Na}(\text{H}_2\text{O})_4]^+ \left[\begin{array}{c} \text{HO} \quad \text{O}-\text{O} \quad \text{OH} \\ \diagdown \quad \quad \diagup \\ \text{B} \quad \quad \text{B} \\ \diagup \quad \quad \diagdown \\ \text{HO} \quad \text{O}-\text{O} \quad \text{OH} \end{array} \right]^{2-}$
Sodium peroxoborate trihydrate	[28962-65-4]	$\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 2 \text{H}_2\text{O}$	disodium di- μ -peroxo-bis(dihydroxoborate) tetrahydrate
Sodium perborate trihydrate	[28108-09-0]	$\text{NaBO}_3 \cdot 3 \text{H}_2\text{O}$	$2 [\text{Na}(\text{H}_2\text{O})_4]^+ \left[\begin{array}{c} \text{HO} \quad \text{O}-\text{O} \quad \text{OH} \\ \diagdown \quad \quad \diagup \\ \text{B} \quad \quad \text{B} \\ \diagup \quad \quad \diagdown \\ \text{HO} \quad \text{O}-\text{O} \quad \text{OH} \end{array} \right]^{2-}$
Sodium peroxoborate monohydrate	[10332-33-9]	$\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$	disodium di- μ -peroxo-bis(dihydroxoborate)
Sodium perborate monohydrate	[15120-21-5]	$\text{NaBO}_3 \cdot \text{H}_2\text{O}$	$2 \text{Na}^+ \left[\begin{array}{c} \text{HO} \quad \text{O}-\text{O} \quad \text{OH} \\ \diagdown \quad \quad \diagup \\ \text{B} \quad \quad \text{B} \\ \diagup \quad \quad \diagdown \\ \text{HO} \quad \text{O}-\text{O} \quad \text{OH} \end{array} \right]^{2-}$
Anhydrous sodium peroxoborate	[7632-04-4]	NaBO_3	not a well-defined compound; sodium borate/boron-oxygen radical

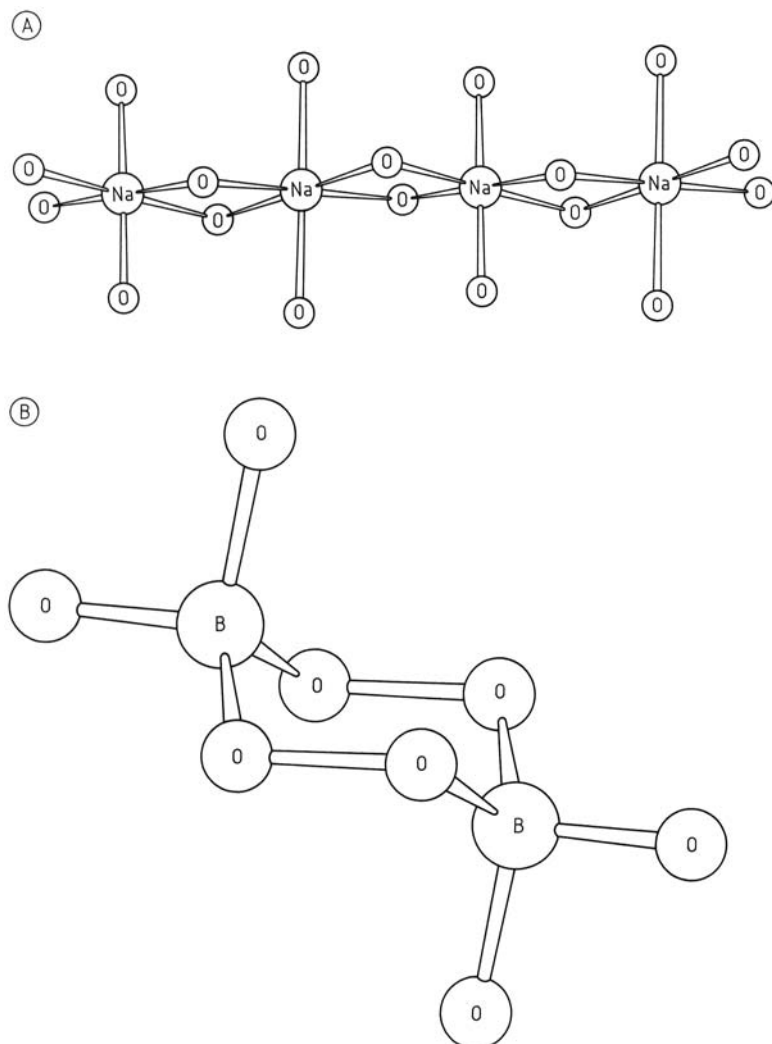


Figure 3. A) Part of the chain of hydrated Na^+ ions in sodium peroxoborate tetrahydrate; B) Structure of the $[\text{BO}_2(\text{OH})_2]^{2-}$ anion

A molecular structure for the anhydride has been discussed in which the six-membered ring is a boron–oxygen radical [38].

Vapor-pressure studies on sodium perborate hydrates [26] have shown that the isotherms for compound formation and decomposition as a function of water vapor partial pressure exhibit marked hysteresis; that is, the sodium perborate hydrates do not behave as classical hydrates, for which the formation and decomposition reactions are reversible.

The thermal decomposition of sodium perborate hydrates has been investigated by

thermogravimetric analysis. The decomposition curves for the tetrahydrate and trihydrate are very similar. At temperatures above 150°C they correspond to the curve obtained with sodium perborate monohydrate [37].

Physical Properties. *Sodium perborate tetrahydrate*, M_r 153.9, ρ 1.731 g/cm^3 , theoretical active oxygen content 10.38 wt%, melts in its own water of crystallization at 65.5°C .

The commercial product is a white, crystalline solid with a spherulitic or elongated particle shape, and a particle size distribution of

0.1–1.0 mm. Depending on the crystal shape, bulk densities of 0.65–0.9 kg/L can be obtained. When stored under cool, dry conditions the rate of loss of active oxygen is only 1 % per year. Decomposition is accelerated at higher temperatures and moisture content. There is a tendency for increased caking at higher temperatures caused by conversion of the tetrahydrate to the trihydrate [39].

The solubility in water is 0.152 mol/L at 20 °C and 0.388 mol/L at 40 °C.

Thermogravimetric analysis curves for sodium perborate tetrahydrate show that decomposition takes place in three stages: 20–150 °C, 150–165 °C, and 165–400 °C. In the first stage, the tetrahydrate is dehydrated to the monohydrate.

Sodium perborate trihydrate, M_r 135.9, ρ 1.86 g/cm³, theoretical active oxygen content 11.8 wt %, melts in its own water of crystallization at 81.7 °C.

Solubility and vapor pressure determinations indicate that above 15 °C sodium perborate trihydrate is the thermodynamically more stable phase. The tetrahydrate is stable below this temperature. However, the transition requires considerable activation energy and therefore only occurs in solution at elevated temperature or upon addition of substances which reduce the solubility [40].

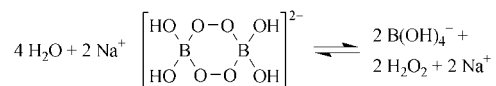
Sodium perborate monohydrate, M_r 99.8, has a theoretical active oxygen content of 16.0 wt %. The anhydrous compound has no definite melting point and decomposes when strongly heated, liberating water and oxygen. The commercial product is manufactured by dehydration of sodium perborate tetrahydrate and is a white crystalline solid with a bulk density of 0.5–0.65 g/cm³, depending on the starting material used. Modern methods of direct synthesis give a product with a bulk density between 0.4 and 1 g/cm³ [41], [42]. A major advantage of sodium perborate monohydrate compared to the tetrahydrate, apart from its higher active oxygen content, is its much higher rate of dissolution, which results in better bleaching performance under short wash cycle conditions. The time required for 2 g tetrahydrate to dissolve in 1 L water at 15 °C is 6–8 min, while the same amount of monohydrate dissolves in < 1 min.

Anhydrous sodium perborate, also known under the trade name Oxoborate, has a theoretical

molecular mass of 81.8. However, the commercial product is heterogeneous and contains ca. 2 wt % residual active oxygen. The releasable oxygen is liberated spontaneously as molecular oxygen when anhydrous sodium perborate comes into contact with water.

The releasable oxygen is determined by adding a weighed amount to dilute sulfuric acid, and measuring the oxygen liberated either gravimetrically or volumetrically. Oxoborate has a pale yellowish color. It is X-ray amorphous, and has paramagnetic properties [43].

Chemical Properties Cryoscopic molecular mass determinations and conductivity measurements show that in aqueous solution the sodium perborate hydrates are partially hydrolyzed, reforming the starting materials metaborate and hydrogen peroxide according to the following equation [37]:



As can be seen from this equation, the amount of free H₂O₂ cannot be determined by titration, since this continually displaces the equilibrium.

The aqueous solution of sodium perborate reacts like an alkaline solution of hydrogen peroxide, the active oxygen content being catalytically decomposed by heavy metal ions. Stabilization can be achieved by adding magnesium salts. The pH is 10.1–10.4 and is virtually independent of the concentration. The active oxygen content can be determined by titration with potassium permanganate in dilute sulfuric acid. The sodium content is measured by titration with hydrochloric acid using methyl orange as the indicator. Finally, the boron content is determined by reacting the solution with a polyhydric alcohol, e.g., glycerine, leading to complex formation and producing a monobasic acid which can be titrated with sodium hydroxide solution using phenolphthalein as the indicator.

3.1.2. Production

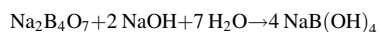
The former electrochemical production of sodium perborate tetrahydrate is no longer of commercial importance [44]. The demand for

higher product quality has led to the development of the process described below, almost the only one used today on a large scale.

Raw Materials The boron-containing raw material is generally a water-soluble sodium tetraborate. Technical-grade borax pentahydrate is used, but impure minerals such as kernite and tincal are also employed.

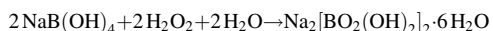
The minerals ulexite (sodium calcium borate), colemanite and pandernite (calcium borates) are also used but to a lesser extent because they must be reacted with sodium carbonate, producing considerable quantities of sludge. The active oxygen component is usually hydrogen peroxide.

Sodium perborate tetrahydrate is produced in a two-stage process (Fig. 4). In the first stage, the boron minerals are reacted with aqueous sodium hydroxide to yield a highly concentrated solution of sodium tetrahydroxoborate:



Recycled mother liquor from the crystallization stage is mixed with sodium hydroxide solution and the boron-containing raw material added, whereby the temperature rises from 60 to 95 °C [45]. Insoluble components are then removed by decantation or filtration. The resulting clear solution containing up to 800 g/L solid

(expressed as NaBO_2) is diluted with more recirculated mother liquor and is subsequently cooled to below 40 °C. In the second stage, the diluted solution of sodium tetrahydroxoborate is treated with hydrogen peroxide with cooling at temperatures below 30 °C. This causes sodium perborate tetrahydrate to precipitate:



The perborate is stabilized by adding a solution of magnesium sulfate or alkali metal or alkaline earth metal silicate, either before or after the crystallization stage [46].

Both the chemical reaction and the crystallization can have several variations. The two components can be reacted continuously in the crystal-free external recirculation zone of a vacuum crystallizer, and then caused to flow through the salt layer, so that the solution is no longer supersaturated [47]. Depending on the raw materials used and the process, different crystal shapes and crystal size distributions can be obtained.

Degussa has described a process for the production of attrition-resistant sodium perborate tetrahydrate crystals. A highly supersaturated solution (200–700 g/L) of sodium perborate is passed into a previously prepared suspension of small crystals. Crystallization initiated by these nuclei yields coarse, compact crystal agglomerates [48].

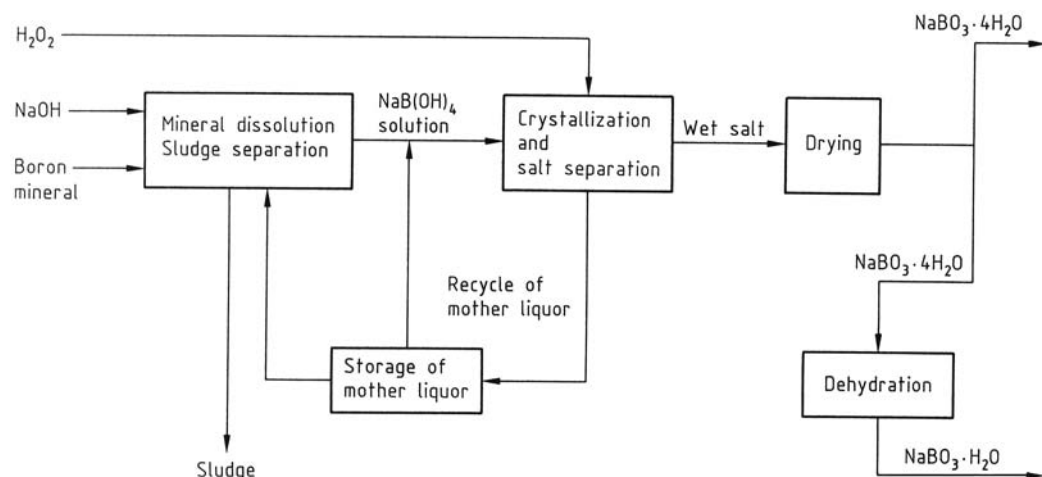


Figure 4. Flow diagram for the production of sodium peroxoborate

Kali-Chemie has reported a continuous process in which controlling the stoichiometry produces attrition-resistant, free-flowing crystals of sodium perborate tetrahydrate with a bulk density of 0.75–0.85 kg/L [49]. Crystallization is carried out in an open, cooled, stirred vessel. The sodium perborate suspension formed is continuously removed and fed at a controlled rate directly into an automatic centrifuge. The mother liquor is recirculated. The separated crystals, containing 3–10 wt % water, are dried in a rotary or fluidized-bed dryer with air at ca. 100 °C [49].

During drying, the temperature of the salt must be kept below 60 °C to prevent melting. After drying, the product is cooled to ca. 25 °C by air in fluidized-bed coolers. Fine particles of perborate are removed from the exhaust air by wet scrubbers, integrated in the mother liquor recirculation system.

Major producers of sodium perborate tetrahydrate are Belinka (Slovenia), Degussa (Belgium, Austria), Etibank (Turkey), FMC Foret (Spain), Solvay (Australia, Germany).

Sodium Perborate Monohydrate is produced by dehydration of sodium perborate tetrahydrate. By removing the water of crystallization with warm air in a fluidized-bed dryer, an attrition-resistant product is obtained. The inlet temperature of the air is maintained between 180 and 210 °C [50].

A highly attrition resistant product is obtained by dehydration under vacuum [51], or in a fluidized-bed dryer operating at a relative humidity of 10–40 % and an air inlet temperature of 100–180 °C [52]. Alternatively a relative humidity of 40–80 % and an air exhaust temperature of at least 60 °C can be employed [53]. Besides the conventional processes with tetrahydrate as an intermediate, new production technologies have been described in which sodium perborate monohydrate is produced directly from aqueous solutions.

According to an Interlox patent, attrition-resistant granules of sodium perborate monohydrate with a bulk density of 0.4–1 kg/L are obtained by spraying solutions of H_2O_2 and NaBO_2 onto a fluidized bed of crystal nuclei at up to 100 °C [42]. The rate of dissolution of these granules is rather low compared to that of monohydrate manufactured by conventional processes but can be improved by adding surface-active agents [54].

Degussa has described the direct synthesis of a sodium perborate monohydrate product with a bulk density of 0.4–1 kg/L. Sodium perborate solution is spray-dried to produce the monohydrate in the form of a fine powder. The fines are then granulated in a fluidized bed or granulated by compression to yield a product with good storage stability and dissolution properties [41].

Major producers of sodium perborate monohydrate are Degussa (Belgium, Austria), FMC Foret (Spain), Solvay (Germany).

Anhydrous Sodium Perborate is produced by further dehydration of sodium perborate monohydrate. Sodium perborate monohydrate is dehydrated in a fluidized bed with dry air at 150–160 °C [56]. The dehydration of the tetrahydrate requires a stepwise, slow temperature increase using dry, CO_2 -free air to avoid agglomeration of the particles in the fluidized bed [57]. Both processes yield products with 15–17 wt % releasable oxygen and 1–2 wt % active oxygen.

3.1.3. Uses

Sodium perborate tetrahydrate and monohydrate are still used with decreasing tendency as active oxygen source in oxidizing and bleaching agents in cleaning, cosmetic, and pharmaceutical products, but mainly in detergents (→ Laundry Detergents). It is estimated that ca. 95 % of the perborates are consumed by this market. Detergents contain up to 30 wt % sodium perborate tetrahydrate and/or up to 15 wt % monohydrate. The monohydrate is preferred if rapid dissolution, improved storage stability, and compatibility with other constituents such as activators and water-softening agents are required. Other applications include detergents for automatic dishwashers, denture cleaners, color-safe bleach powders, and hair-treatment preparations. Sodium perborate has been used as a slow-release oxygen source in heap leaching of gold and silver ores [55].

Anhydrous sodium perborate is mainly used in denture cleanser tablets to enhance dissolution and to produce effervescence.

In 1998 the world production capacity for perborates (as sodium perborate tetrahydrate) was estimated at 550 000 t of which approximately 85 % was produced in Europe. With

changes in European environmental policy and the discussion on the ecotoxicological properties of borates and perborates at the end of the 20th century, a continuous shift from sodium perborates to sodium carbonate peroxohydrate took place, and this entailed a significant reduction in production capacity estimated in 2004 to be less than 300 000 t. Especially Solvay converted existing sodium perborate production facilities to sodium carbonate peroxohydrate production.

3.1.4. Product Specifications

Commercial sodium perborate tetrahydrate and monohydrate have an active oxygen content of at least 10 and 15 wt %, respectively. They are white, odorless, free-flowing salts with a particle size distribution of 95 % between 0.1 and 1.0 mm. Modifications in the production process can give bulk densities for the tetrahydrate between 0.65 and 0.85 kg/L, and for the monohydrate between 0.50 and 0.65 kg/L. With storage under cool, dry conditions, the annual active oxygen loss rate is < 2 % (relative). The dissolution time for 2 g substance in 1 L water is ca. 6–8 min for the tetrahydrate and < 1 min for the monohydrate. The residual moisture content, determined by drying for 30 min at 60 °C in a vacuum, should not exceed 1 wt % for the monohydrate. Attrition resistance is an important parameter and should not be higher than 10 % according to ISO 5937.

Commercial anhydrous sodium perborate has at least 13.0 wt % releasable oxygen and ca. 1.5–2.5 wt % active oxygen. It also contains small amounts of sodium perborate monohydrate and sodium metaborate, depending on the production process. The light yellow salt has a particle size distribution of ca. 90 wt % between 0.1 and 1.0 mm and a bulk density between 0.3 and 0.4 kg/L. It dissolves readily in water with evolution of oxygen.

3.1.5. Storage and Transportation

Sodium perborates must be stored under cool, dry conditions. Exothermic decomposition with liberation of oxygen can be caused by heat, moisture, and/or contact with decomposition catalysts, e.g., heavy metals, alkali, or dirt.

Adiabatic storage conditions can lead to self-accelerating decomposition of sodium perborate monohydrate.

After manufacture, sodium perborate tetrahydrate and monohydrate may be stored in silos and transported in bulk by rail or truck or packed in paper sacks, optionally with polyethylene inner liners, or in polyethylene sacks. Oxoborate (anhydrous sodium perborate) is transported only in polyethylene-lined paper sacks.

Sodium perborate tetrahydrate is considered nonhazardous for international transportation purposes. Due to a change in testing methods for oxidizing substances, the UN classification for sodium perborate monohydrate changed recently to Oxidizer 5.1. [59]. Oxoborate has been assigned UN No. 3247 and is also classified as a Class 5.1 oxidizing substance.

3.2. Other Peroxoborates

MELIKOFF and PISSARJEWSKI prepared peroxoborates of magnesium, calcium, barium, and strontium in 1898. Production processes for potassium peroxoborate [58], [60] and the peroxoborates of the alkaline earth metals have been described in patents [61]. Novel peroxoborates with monovalent cations and considerable molar excess of H_2O_2 have been published by HELLER and PAWEŁ [62]. However, these compounds now have no commercial importance.

4. Peroxosulfuric Acids and Peroxosulfates

Peroxomonosulfuric acid and peroxodisulfuric acid are intermediates in the former electrochemical production of hydrogen peroxide (\rightarrow Hydrogen Peroxide, Section 4.3.). Peroxodisulfuric acid is not of commercial importance. However, its salts, the peroxodisulfates, are widely used as active oxygen carriers and oxidizing agents. Industrially important salts of peroxodisulfuric acid are those of ammonium [7727-54-0], sodium [7775-27-1], and potassium [7727-21-1].

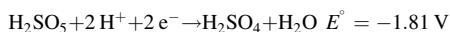
Peroxomonosulfuric H_2SO_5 in the form of Caro's acid has found industrial applications in the mining industry and in pulp bleaching. The salts of peroxomonosulfuric acid include the peroxomonosulfates of the alkali, alkaline earth,

and other metals [63], e.g., KHSO_5 [25482-78-4] [64], and the triple salt $2 \text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ [37222-66-5] [65], which is sold under the trade names Caroat (Degussa) and Oxone (DuPont).

4.1. Peroxomonosulfuric Acid

Peroxomonosulfuric acid [7722-86-3] is a colorless crystalline solid, *mp* 45 °C, that is difficult to prepare in high purity. Solutions of Caro's acid lose active oxygen significantly faster than hydrogen peroxide solutions. The stability of peroxomonosulfuric acid solutions increases with decreasing concentration and residual H_2O_2 content [66]. Peroxomonosulfuric acid is a strong acid. The proton bound to the peroxo group is, like that in H_2O_2 , a weak acid with a $\text{p}K_a$ of 9.4. In the presence of water it hydrolyzes rapidly yielding H_2O_2 and sulfuric acid.

Peroxomonosulfuric acid is a powerful oxidizing agent:

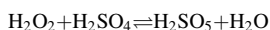


The oxidation potential of peroxomonosulfuric acid was determined by a thermodynamic method to be 1.81 V [67], [68]. It oxidizes cyanide to cyanate, chloride to chlorine, sulfide to sulfate, and formaldehyde to H_2 and formic acid. Under neutral and alkaline conditions, peroxomonosulfate oxidizes hydrogen peroxide yielding oxygen gas. Peroxomonosulfuric acid exhibits significantly better bactericidal properties than H_2O_2 and has good overall effectiveness against bacteria and viruses, in particular under weakly acidic conditions [69].

4.2. Caro's Acid

Caro's acid is named after HEINRICH CARO (1834–1910) who first described its synthesis and properties in 1898.

Production Caro's acid obtained by treating sulfuric acid with hydrogen peroxide is an equilibrium mixture of peroxomonosulfuric acid, hydrogen peroxide, sulfuric acid, and water. The equilibrium constant for this reaction is 0.1 [70].



The highly exothermic reaction requires removal of the heat of reaction to give high yields of peroxomonosulfuric acid. There are two manufacturing technologies: the isothermal and the adiabatic process.

In the *isothermal process*, 70 % H_2O_2 is mixed with 93–98 % sulfuric acid with efficient heat removal, so that the temperature does not exceed 15–30 °C. If equimolar quantities of reactants are employed, the product contains 42–50 % H_2SO_5 and ca. 10 % H_2O_2 . H_2SO_5 yields can be significantly increased by increasing the amount of H_2SO_4 or by using oleum. Degussa describes an on-site manufacturing process in which H_2O_2 is added in separate reaction stages in series resulting in ca. 15 % higher yields over conventional single-stage reactors when a 2:1 molar ratio of H_2SO_4 (96–98 %) and H_2O_2 (70 %) is employed [71], [72].

In the *adiabatic process*, the reactants are mixed rapidly in a small-volume, high-throughput static mixer without cooling. Several patents describe various designs of equipment for adiabatic generation of Caro's acid [73–77]. Typically, the yields of Caro's acid with this method are in the range of 25–45 %. A process for the production of stable aqueous sodium peroxomonosulfate solutions has been described by Degussa [66].

Uses Due to new and cost-effective on-site generation technologies, Caro's acid has found increasing use in mining and hydrometallurgy, pulp bleaching, and the electronics industry.

In the mining industry, Caro's acid is used as a detoxifying agent for residual cyanide in the tailings from gold and silver ore processing. Due to its faster oxidation kinetics and oxidizing power, Caro's acid has several advantages over catalyzed H_2O_2 (e.g., it also oxidizes thiocyanate). This application is practiced at several gold mines in North America [78–82]. Caro's acid also has been described as an oxidant in uranium ore processing.

In the pulp and paper industry, Caro's acid has proved to be an effective delignification chemical in totally chlorine free bleaching sequences; it replaces chlorine and chlorine dioxide. When employed under controlled pH and temperature conditions, the mechanical properties of the

cellulose fibers are not impaired [83–86]. DuPont describes a delignification process using a combination of Caro's acid and peracetic acid [87], [88]. Caro's acid is also the starting material for the manufacture of peroxomonosulfates (see Section 4.3.2).

A proprietary form of Caro's acid is marketed in the electronics industry under the name of Nanostrip. It is used for cleaning and reclaiming of silicon wafers. Manufacturers are Cyantech (US), Micro-Image Technologies (UK), and RASA Industries (Japan).

4.3. Peroxomonosulfates

4.3.1. Properties

A number of sodium, potassium, ammonium, cesium, lithium, and rubidium salts of peroxomonosulfuric acid have been described in the literature. Only the potassium salt in the form of the triple salt $2 \text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, M_r 614.8, ρ 2.313 g/cm³, theoretical active oxygen content 5.2 wt %, has gained commercial importance. Recent X-ray structure analysis investigations [89] have shown that it crystallizes in the monoclinic system, contrary to earlier reports describing an orthorhombic structure [65]. The crystal lattice consists of an array of K^+ cations and $\text{H}_3\text{S}_4\text{O}_{18}^{5-}$ anions in which HSO_5^- , HSO_4^- and SO_4^{2-} units are also included (Fig. 5).

The commercial product is a white, odorless, free-flowing material with a bulk density of 1–1.2 kg/L. About 90 wt % is in the particle size range 0.1–0.8 mm. Under proper storage conditions, the loss of active oxygen is < 1 % per month. The triple salt is soluble in water (25 g/L H_2O at 20 °C) and dissolves rapidly. The pH of an 1 wt % solution is ca. 2.3. The bactericidal properties of the triple salt are summarized in [90].

The triple salt is classified by the UN as corrosive solid under UN No. 3260.

4.3.2. Production

The starting materials are sulfuric acid or oleum, hydrogen peroxide, and potassium hydroxide. In the first step, hydrogen peroxide (65–90 wt %) and oleum (53–82 wt %) in a molar ratio of 1:1.3–2.7 are continuously mixed in a cooled reaction vessel at a temperature below 8 °C to obtain a 37–66 wt % peroxomonosulfuric acid containing H_2SO_4 , H_2O , and H_2O_2 [91].

In the second stage the mixture is partially neutralized with potassium hydroxide and the triple salt is crystallized. This step requires careful control of the mother liquor composition to obtain high yields [65] (see Fig. 6).

According to a patent of the former Peroxid-Chemie (today Degussa), peroxomonosulfuric acid is produced from H_2SO_4 (90–100 wt %) and

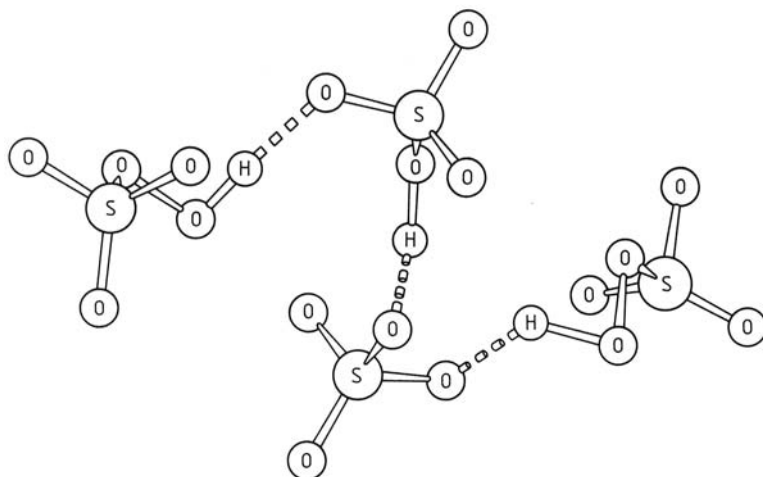


Figure 5. Arrangement of the complex anions in the compound $2 \text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$

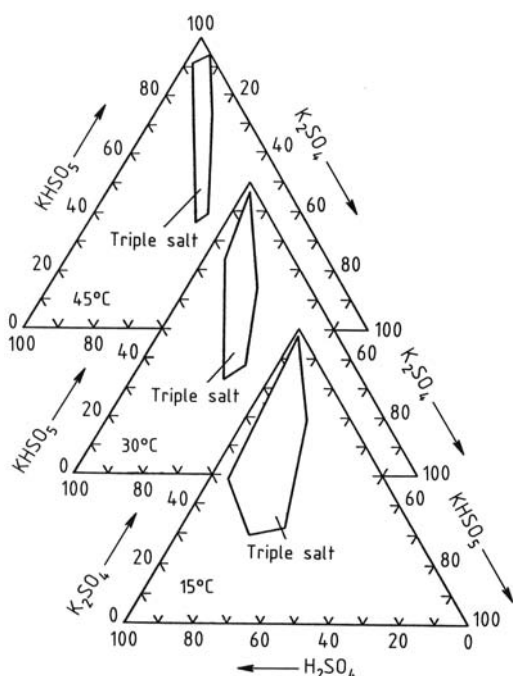


Figure 6. Region of stability of the triple salt $2 \text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ as a function of the composition of the mother liquor and temperature

H_2O_2 (30–90 wt %), and then continuously fed, together with a concentrated solution of potassium hydroxide, into a circulating mother liquor containing 25–30 wt % KHSO_5 and ca. 15 wt % H_2SO_4 or K_2SO_4 in aqueous solution [92]. The water introduced with the raw materials and formed in the neutralization reaction is removed by passing the reaction mixture through vacuum treatment equipment at ca. 25 °C and 1 kPa. Some of the circulating liquor is continuously removed and cooled to ca. 5 °C in a crystallizing vessel, resulting in precipitation of the triple salt.

The salt is isolated by centrifugation, and the mother liquor is fed back into the circulating solution. The filter cake is washed while in the centrifuge, and the wet salt is dried in a fluidized-bed dryer [92]. The product is packed in polyethylene-lined plastic sacks and is stored under cool, dry conditions.

4.3.3. Uses

Peroxomonosulfate triple salt is used because of its powerful oxidizing properties and bactericidal

effects in surface cleaners and dishwashing powders to improve bleaching and disinfecting action, especially at low temperatures [93–95]. Ketones have been reported to enhance the bleaching power of peroxomonosulfates by in situ formation of highly reactive dioxiranes [96–98].

A major use of the triple salt is in denture cleaners. In combination with sodium perborate monohydrate it gives an effervescence due to reaction with perborate yielding oxygen gas under alkaline conditions. In more recent formulations of denture cleaners Carcoat is also combined with sodium percarbonate instead of sodium perborate monohydrate. The triple salt is used in the textile industry for nonshrinking and nonfelting treatment of wool, and in the electrical industry for etching printed circuits. In the electroplating and metal finishing industry, potassium peroxomonosulfate triple salt is employed for the treatment of cyanide-containing industrial wastewater and as a mild etchant and pickling agent [99], [100].

In water treatment it has found application as a shock treatment agent for swimming pool water [101]. It quickly oxidizes malodorous chloramines to nitrogen and nitrate.

Another application is its use in wastepaper recycling for destruction of wet-strength resin [102].

4.3.4. Analysis

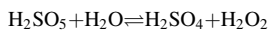
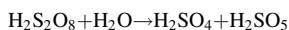
Peroxomonosulfuric acid can be determined in the presence of H_2O_2 and peroxodisulfuric acid by redox titration, based on the reaction of the H_2SO_5 with arsenic acid and subsequent titration of the residual H_2O_2 with cerium(IV) sulfate solution. The peroxodisulfuric acid is determined by the addition of arsenic acid and ICl and titration of excess arsenic acid with $\text{Ce}(\text{SO}_4)_2$ [103].

5. Peroxodisulfuric Acid and Peroxodisulfates

5.1. Properties

The dibasic peroxodisulfuric acid [13445-49-3] also known as Marshall's acid, $\text{HO}_3\text{SOOSO}_3\text{H}$, forms white crystals (*mp* 65°C decomp.).

The hydrolysis of peroxodisulfuric acid to sulfuric acid and peroxomonosulfuric acid is irreversible, while further hydrolysis of peroxomonosulfuric acid is reversible:



The hydrolysis of peroxodisulfuric acid is favored by increasing temperature and acid concentration [104–107]. Sulfate radicals are postulated as an unstable intermediate [108]. The peroxodisulfate ion in aqueous solution is one of the most powerful oxidizing agents ($E^0 = 2.05 \text{ V}$) [109].

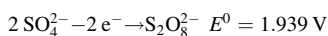
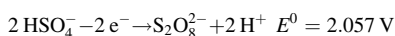
The peroxodisulfates of ammonium, sodium, and potassium are white, crystalline, and stable under dry conditions. The salts decompose on heating in two steps: first the formation of pyrosulfates and oxygen and then upon further heating the decomposition of the pyrosulfate into sulfate and sulfur tri- and dioxide [110], [111]. The decomposition temperatures increase in the series $\text{NH}_4^+ < \text{K}^+ < \text{Na}^+$, and decrease with increasing moisture content. Mixtures with combustible materials are easily ignited and burn vigorously even in the absence of oxygen.

In aqueous solution, the salts are hydrolyzed in a similar manner to peroxodisulfuric acid. Aqueous solutions of peroxodisulfates are slightly acidic (25 wt % $(\text{NH}_4)_2\text{S}_2\text{O}_8$, pH 2.30; 25 wt % $\text{Na}_2\text{S}_2\text{O}_8$, pH 4.35). Solubilities at 20 °C in 100 cm³ water are: ammonium peroxodisulfate 55.9 g, sodium peroxodisulfate 55.6 g, and potassium peroxodisulfate 5.0 g.

5.2. Production

Pure peroxodisulfuric acid is formed under the same conditions as peroxomonosulfuric acid, i.e., from chlorosulfuric acid and hydrogen peroxide [112]. It has no industrial application.

Aqueous solutions of peroxodisulfuric acid are manufactured by anodic oxidation of sulfuric acid:



This electrochemical synthesis followed by hydrolysis was formerly the most important industrial

manufacturing method for hydrogen peroxide before the development of the autoxidation process.

The electrode process to form $\text{S}_2\text{O}_8^{2-}$ is complex [113], [114] and is accompanied by the undesired evolution of oxygen. To minimize the evolution of oxygen, electrolysis is performed at high current densities [115] with electrodes having a high oxygen overpotential, e.g., platinum. In addition, potential-increasing substances, e.g., halides or pseudohalides, are added to the electrolyte [116], [117]. The most important process that lowers the current yield is the thermodynamically favored acid-catalyzed hydrolysis of the peroxodisulfate anion to give peroxomonosulfate, whose anodic reaction leads to increased evolution of oxygen [118]. Therefore, the following requirements for the design have to be considered in order to achieve a high current efficiency:

1. Short residence time in the cell, no backmixing of the anolyte, but high final concentration of the product
2. High anodic current density with minimum heating of the electrolyte
3. Effective dissipation of heat through heat exchangers with large surface areas
4. Small anolyte gap to minimize voltage losses
5. Dimensionally stable anode construction with minimum use of platinum

The first successful industrial realization was the Degussa–Weissenstein cell [119]. A further development is a bipolar electrolyzer [120–122] with ion-exchange membranes [123], which is reviewed in [124], [125]. A bipolar electrode plate (see Fig. 7) is the basic element in the filter-press electrolysis cell, which consists of 26 electrodes [124], [126]. The characteristic feature is the large number of vertical, parallel anolyte channels ($9 \times 3 \text{ mm}$). The anodes are ribbonlike platinum foils on a carrier, which is cooled from behind. Anolyte and catholyte are separated by a microporous polymer diaphragm or, in a more recent development, by a cation-exchange membrane [127].

The electrolytic conditions for the production of crystalline peroxodisulfate salts are determined by the solubilities of the starting materials and products in the electrolytes, and these in turn are dependent on the proton activity. Fundamental investigations are reported in [128–138].

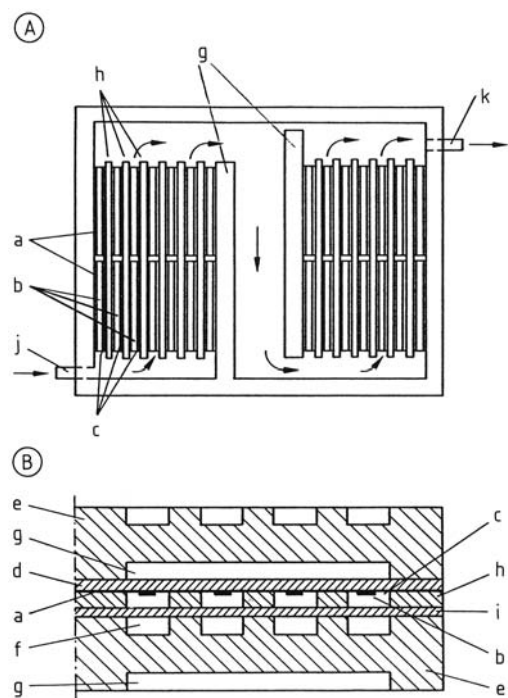


Figure 7. Schematic view of a frame and plate electrolyzer A) Anode plate; B) Cross-sectional view a) Tantalum foil; b) Platinum foil strip anodes; c) Anode channel; d) Supporting plate; e) Graphite cathode block; f) Cathode channel; g) Cooling channel; h) Spacer; i) Diaphragm; j) Anolyte inlet; k) Anolyte outlet

The current efficiency increases in the series $H^+ < Li^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+$ due to the electrostatic effects of the cations in the electrolytic double layer at the electrode/electrolyte phase boundary [139]. The most favorable conditions with respect to solubility ratios and cationic effects are those associated with the production of ammonium peroxodisulfate. Therefore, the ammonium salt is still the most important peroxodisulfate produced electrolytically.

Figure 8 shows a flow diagram for the manufacture of ammonium and sodium peroxodisulfates. During electrolysis ammonium ions and water of hydration enrich the catholyte by migration through the diaphragm. The resulting catholyte excess is mixed with the anolyte to replace the consumed sulfate. After crystallization and separation of ammonium peroxodisulfate, the residual solution is neutralized with ammonia.

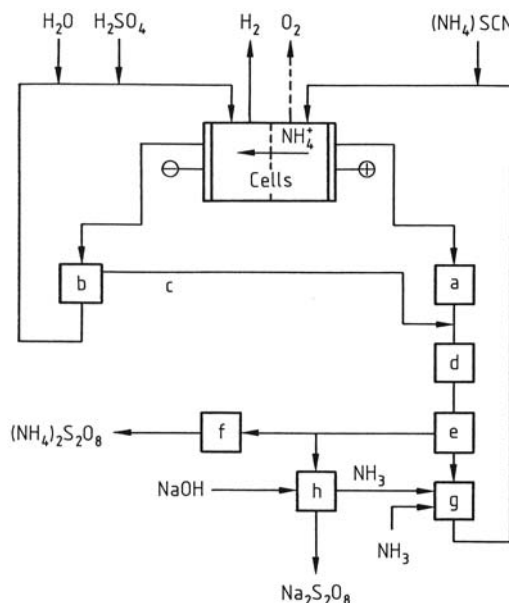


Figure 8. Flow sheet of an ammonium and sodium peroxodisulfate production plant a) Anolyte; b) Catholyte; c) Overflow; d) Vacuum crystallization; e) Centrifuge; f) Drying; g) Neutralization of mother liquor; h) Reactor and ammonia stripping

Typical operational data for the production of ammonium peroxodisulfate are as follows:

Current density, A/m ²	0.5–1
Cell voltage, V	4–6
Current efficiency, %	75–90
Specific energy consumption, kW · h/kg	1–2
Electrolyte temperature in anolyte, °C	30–45
Anolyte concentrations, g/L	
Inlet cell	
(NH ₄) ₂ SO ₄	380–440
(NH ₄) ₂ S ₂ O ₈	100–160
H ₂ SO ₄	0–150
(NH ₄)SCN	0.05–0.40
Exit cell	
(NH ₄) ₂ S ₂ O ₈	300–350
H ₂ SO ₄	10–150
(NH ₄) ₂ SO ₄	200–240
Catholyte concentration, g/L	
H ₂ SO ₄	300–700
(NH ₄) ₂ SO ₄	300–550

The electrolytic process is described in [140]. Details of the conversion of ammonium peroxodisulfate to the sodium [141] and potassium [142] salts are given in [143]. Additionally

methods for direct electrochemical synthesis of the sodium and potassium salts have been published [144–148]. The advantage of these methods is that special equipment for handling ammonia is not required. However, in the direct electrochemical synthesis of sodium and potassium peroxodisulfates, special conditions for the electrolyte concentration and composition have to be considered to avoid solubility and electrolysis problems [146–150].

5.3. Uses

The worldwide production capacity of peroxodisulfates in 2005 was estimated to be 165 000 t. The most important manufacturers are FMC (USA), Degussa (Germany), RheinPerChemie (Germany), and Mitsubishi Gas Chemical (Japan). Several smaller manufacturers are located in China, where additional capacities are about to be installed. The two largest market segments for peroxodisulfates are polymer production and metal etching, accounting for 85 % of the total market.

Peroxodisulfates are employed as radical initiators in combination with reducing agents and cocatalysts in emulsion polymerization processes for the manufacture of acrylonitrile–butadiene–styrene copolymers (ABS), high-impact polystyrene (HIPS), and styrene–acrylonitrile (SAN) [151], [152]. Redox systems that are commonly used in combination with peroxodisulfates are described in [153].

In the electronics industry peroxodisulfates are employed for etching printed circuit boards and removal of photoresists [154–156].

Peroxodisulfates have long been employed for desizing textile goods. A new application is as a bleaching agent in denim finishing [157–160].

A very important market are hair-coloring formulations which contain peroxodisulfates as the active ingredient [161], [162].

Sodium peroxodisulfate-based formulations are marketed as shock-treatment chemicals for swimming pool water [163], [164]. Peroxodisulfates are used in the preparation of adjustable-viscosity starch derivatives [165]. Peroxodisulfates have found also application in wastepaper recycling for the oxidation of wet strength resins [166]. An emerging new application is the purification of contaminated soil [167].

Peroxodisulfates have been described as oxidizing agents for photographic fixing baths [168–170].

5.4. Analysis

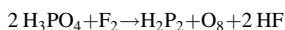
Peroxodisulfate is determined by oxidimetric titration with access of Fe^{2+} (e.g., iron(II) sulfate solution) and back-titration with potassium permanganate [171]. For mixtures with other sulfur compounds, separation by ion chromatography is used [172].

6. Peroxophosphoric Acids and Their Salts

The peroxophosphoric acids are structurally similar to the peroxosulfuric acids and behave similarly. They are hydrolyzed more rapidly than the peroxosulfuric acids, but the oxidation reactions of their anions are kinetically inhibited.

Peroxomonophosphoric Acid [13598-52-2], H_3PO_5 , is obtained by reacting phosphorus(V) oxide with hydrogen peroxide [173], [174]. The reaction proceeds less vigorously if the P_2O_5 has been heat-treated at 350–700 °C [175] or is suspended in an inert solvent [176]. A product containing 88 wt % H_3PO_5 and 9.6 wt % H_2O_2 is obtained. Peroxophosphoric acid is a colorless, viscous liquid. The three ionization constants are $\text{p}K_1 = 1.1$, $\text{p}K_2 = 5.5$ and $\text{p}K_3 = 12.8$ [177]. The salts can be obtained by neutralization, e.g., with potassium hydroxide, which produces the relatively stable, crystallizable, but hygroscopic salt KH_2PO_5 [176–179].

Peroxodiphosphoric Acid [13825-81-5], $\text{H}_4\text{P}_2\text{O}_8$, can be prepared by anodic oxidation of phosphoric acid. A mixture of peroxodiphosphoric and peroxomonophosphoric acid is obtained by reacting cold phosphoric acid with fluorine.



Peroxodiphosphoric acid is not produced commercially. Several salts have been reported, but only tetrapotassium peroxophosphate has been produced on a commercial scale.

Peroxodiphosphates. Potassium peroxodiphosphate $K_4P_2O_8$ [15593-49-4], is prepared by electrolysis of potassium phosphate solutions containing added halide or pseudohalide anions [180]. In the older literature, fluorides are mainly recommended for this, but they cause corrosion problems [181]. Nitrates have been successfully tested as an alternative [182]. The electrolytic technique is analogous to that used in the manufacture of peroxodisulfates (see Section 4.3.2) [183], [184]. Sodium and ammonium peroxodiphosphates are obtained by reacting $K_4P_2O_8$ with the corresponding perchlorates, sometimes in the presence of free perchloric acid [185]. Only the secondary and quaternary peroxodiphosphates are obtainable in a crystalline state, with 6 or 18 molecules of water of crystallization. The hexahydrates can be dehydrated under vacuum at 65 °C. Mixed salts such as $K_2(NH_4)_2P_2O_8$ can be obtained by salting out after partial removal of the potassium ions as $KClO_4$ [186].

Potassium peroxodiphosphate is very soluble in water; a saturated solution of $K_4P_2O_8$ contains 42 wt % at 0 °C, 45 wt % at 25 °C, and 51 wt % at 45 °C. The peroxodiphosphates begin to lose oxygen on heating above 200 °C. The potassium salt is the most stable peroxodiphosphate compound [187–189]. In solution, the $P_2O_8^{4-}$ ions undergo hydrolysis, which is accelerated in the presence of acids [190]. It is a strong oxidizing agent with an oxidation potential of 2.07 V.

The peroxophosphates have very few uses compared to the other peroxo compounds. They have been described as oxidizing agents in cosmetic hair preparations (bleaching, waving, and coloring agents) [191], as etchants for metal surfaces (e.g., aluminum) [192], and radical initiators in the graft polymerization of acrylic and vinylic monomers. However, today peroxophosphates have no commercial use due to their slower reaction kinetics and higher costs compared to the peroxosulfates.

7. Hydrogen Peroxide Addition Compounds

The hydrogen peroxide addition compounds of industrial importance are sodium carbonate peroxohydrate (sodium percarbonate) and urea peroxide (trade name: Percarbamid).

7.1. Sodium Carbonate Peroxohydrate

7.1.1. Properties

Sodium carbonate peroxohydrate [15630-89-4], sodium percarbonate, $Na_2CO_3 \cdot 1.5 H_2O_2$, M_r 157.0, ρ 2.14 g/cm³, is a white salt with an orthorhombic unit cell [193]. Commercial crystallized sodium percarbonate consists of coarse, compact grains with a regular spherulitic crystal form [194]. The bulk density can range from 800 to 1200 g/L, depending on the synthesis conditions. The solubility in 100 mL water is 13.1 g at 10 °C, 15.4 g at 20 °C and 18.0 g at 30 °C [195]. The solubility of sodium percarbonate is reduced in the presence of other salts such as Na_2CO_3 , Na_2SO_4 , and NaCl.

The active oxygen content of technical sodium percarbonate varies between 12.0 wt % and 14.5 wt % (theoretical: 15.28 wt %), depending on the manufacturing process and stabilizing technology.

In contrast to sodium perborate, sodium carbonate peroxohydrate is an addition compound of hydrogen peroxide and sodium carbonate in which the hydrogen peroxide molecule is only weakly bound to the carbonate ion via hydrogen bonding, similar to water of crystallization. Thus, hydrogen peroxide is much more likely to be liberated from sodium carbonate peroxohydrate, for example, in the presence of moisture. Figure 9 shows a computer model of crystalline sodium carbonate peroxohydrate.

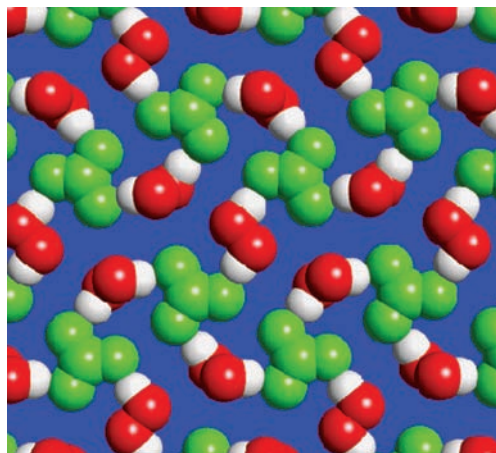


Figure 9. Computer model of crystalline sodium carbonate peroxohydrate

When stored under cool, dry conditions, the rate of active oxygen loss is less than 0.3 % (relative) per month [195]. However, even in the presence of stabilizers, it is much more sensitive to higher temperatures and moisture than sodium perborate. Uncoated sodium percarbonate loses 82–86 % of the active oxygen within 10 d at a relative humidity of 96 % and a temperature of 30 °C [196], whereas sodium perborates loses < 2 %.

The stability of sodium carbonate peroxohydrate is mainly dependent on the presence of water. With increasing humidity the stability decreases as a result of accelerated exchange of the bonded hydrogen peroxide versus water. At the same time, exothermic decomposition of the liberated hydrogen peroxide in the sodium carbonate peroxohydrate, triggered by the caustic environment, yields molecular oxygen and water. Due to the weak bonding of hydrogen peroxide in the crystal lattice of sodium carbonate peroxohydrate, the process of lattice exchange is highly temperature dependent and thus can result in an autocatalytic decomposition reaction, especially if the material is not stabilized properly.

On dissolution of sodium carbonate peroxohydrate in water, the aqueous solution behaves like an alkaline solution of hydrogen peroxide.

Reliable methods for the determination of the decomposition properties of different sodium carbonate peroxohydrate qualities are highly sensitive microcalorimetric measurement methods such as thermal activity monitoring (TAM). Under isothermal conditions, the heat of reaction of the decomposition is measured at a defined temperature as a function of time [197]. The specific thermal output, normally measured in $\mu\text{W/g}$, is specified at less than 10 to ensure safe storage and handling.

The active oxygen content can be determined by titration with potassium permanganate solution in dilute sulfuric acid or by titration with cerium(IV) sulfate solution. The sodium content is obtained by titration with hydrochloric acid with methyl orange as indicator.

7.1.2. Production

Sodium percarbonate was first prepared by TANATAR in 1899 from hydrogen peroxide and soda ash. The product was isolated by precipita-

tion with ethanol. It was not correctly identified as a hydrogen peroxide addition compound until 1909, when RIESENFELD and REINOLD elucidated its structure [198]. Three major processes are used for the industrial manufacture of sodium percarbonate, yielding products with different properties with regard to bulk density, active oxygen content, and stability.

Crystallization Processes. In these processes the production of sodium percarbonate is mainly carried out by crystallization from aqueous solution in continuous or discontinuous manner. A concentrated and filtered solution of sodium carbonate is mixed with a concentrated aqueous solution of hydrogen peroxide, generally stabilized with magnesium salts or alkali metal silicates, in a crystallizer at 10–20 °C. The crystallizer has a clarification zone situated above a stirred zone across which an ascending current of supersaturated sodium carbonate peroxohydrate solution flows. Precipitating particles [199] move countercurrently as a result of gravity and are eluted into a classifier located directly below the crystallizer. The accumulated material at the bottom of the classifier is then removed with a rake. To improve the efficacy of the process salting-out agents like sodium chloride and crystallization aids such as polyphosphates or polyacrylates are used [194, 200–203].

The product is obtained as coarse, mechanically stable crystals (Fig. 10), which are centrifuged followed by drying, preferably in a fluidized-bed dryer with an air inlet temperature of 75 – 130 °C. The mother liquor from the centrifuge can be further concentrated [204] and mixed with industrial-grade sodium carbonate (sometimes after adding a magnesium salt), filtered to remove iron compounds, and fed back into the crystallizer [205].

Processes which do not include a salting-out process with sodium chloride [204], [205] are usually less economic because of the lower space–time yield. Solvay describes a process without a salting-out agent, which yields a coarse sodium percarbonate product with enhanced thermal stability over products produced employing sodium chloride as salting-out agent [206].

Spraying Processes. Several spraying processes for sodium percarbonate are described in

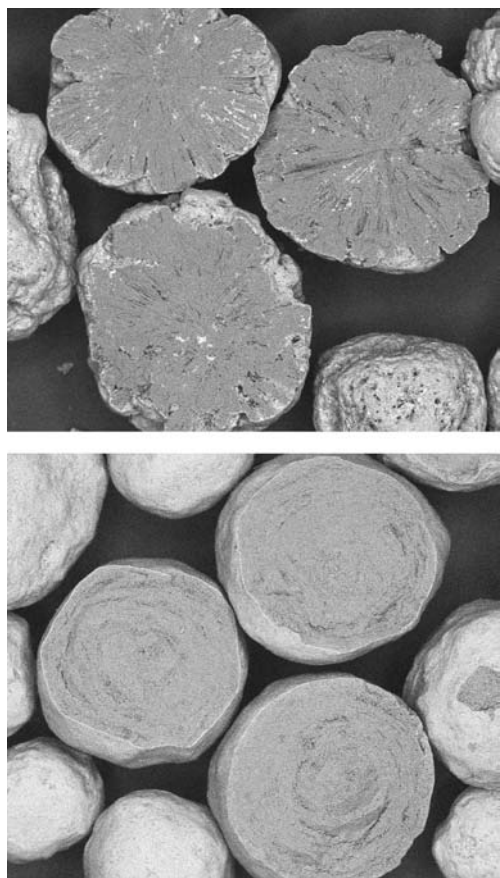


Figure 10. SEM pictures of sodium carbonate peroxohydrate. Top: Sodium carbonate peroxohydrate produced by a crystallization process with radial beamlike crystal growth lines. Bottom: sodium carbonate peroxohydrate produced by a spray-granulation process with onionlike growth structure.

the patent literature. These processes avoid the need for filtration and centrifugation of the crystalline product, and hence less waste is produced during production. In an early process described by Laporte, an aqueous solution or suspension of sodium carbonate and hydrogen peroxide is completely evaporated in a spray dryer [207], [208]. The product has a very low bulk density (ca. 0.35 kg/L) [208]. In further variations and optimizations of this process, described by Solvay, solutions of Na_2CO_3 and H_2O_2 are continuously sprayed separately onto a bed of sodium percarbonate fluidized with hot air [209]. Interlox describes an improved continuous spray granulation process with higher hydrogen peroxide yields by using a single nozzle for both solutions. To ensure a long lifetime of the nozzle the

addition of crystallization inhibitors like sodium hexametaphosphate to the feed solutions is critical [210].

In another process variation, Degussa describes a continuous spray-granulation process in a fluidized-bed reactor using a three-way nozzle. According to a patent [211], the previously necessary use of phosphorous-containing crystallization inhibitors to prevent blockages and incrustations in and on the nozzle can be avoided if the solutions are sprayed through a single three-substance pulverization nozzle with external mixing of the solutions. A highly attrition resistant product with an active oxygen content of $> 14\%$ is obtained [211]. Sodium carbonate peroxohydrate produced by a spray-granulation process is shown in Figure 10.

Dry Methods. In these processes, anhydrous or hydrated sodium carbonate (75–90 wt % Na_2CO_3) is treated with a concentrated solution (50–80 wt %) of hydrogen peroxide, so that only a small amount of water must be removed. This can be achieved in a mixer [212, 213] or in a fluidized-bed reactor [214], in which gaseous hydrogen peroxide can be used [215]. Apart from the long reaction time, these dry processes have the disadvantage that no purification of the sodium carbonate takes place, and therefore these sodium percarbonate products have only moderate storage properties. However, this problem can be solved by recrystallizing the sodium carbonate before use and by using sodium carbonate monohydrate [214]. FMC describes the use of phosphonic acids as additional stabilizers in the synthesis of sodium carbonate peroxohydrate, yielding a product with an active oxygen content of 11–14 % and improved stability [216].

7.1.3. Stabilization, Storage, Packaging, and Transportation

Active-oxygen-containing compounds have a pronounced tendency to decompose in an autocatalytic (self-accelerated) exothermic reaction. Sodium carbonate peroxohydrate is no exception and decomposes into molecular oxygen, water, and soda ash. There are two ways to stabilize sodium percarbonate. One is to improve the stability of the product (core or intrinsic stability)

during the reaction process. The second is to stabilize the product by a separate protective coating to prevent moisture and other incompatible materials coming into direct contact with the peroxohydrate.

Intrinsic Stabilization. On the one hand, the intrinsic stability of sodium carbonate peroxohydrate is affected by the presence of heavy-metal impurities introduced by the raw materials sodium carbonate and hydrogen peroxide. Thus, precipitating agents such as silicates [217, 218] and/or magnesium salts [219], or complexing agents such as phosphates, and phosphonic acid [216], are commonly used. On the other hand, the intrinsic stability is also affected by the presence of excess water, mainly bound as crystal water in unconverted sodium carbonate hydrate or sodium hydrogencarbonate. Proper drying of the finished granulate can significantly improve the stability and reduce the decomposition tendency of sodium carbonate peroxohydrate [220].

Outer Stabilization. The outer stabilization of sodium carbonate peroxohydrate is necessary to improve the stability of the material in the presence of other detergent components. Especially protection against moisture brought into the detergent formulation by other ingredients is critical, since uncontrolled interaction of water with sodium carbonate peroxohydrate can result in loss of the active component. During production the absence of a coating or an insufficient coating can cause severe autocatalytic decomposition reactions accompanied by a strong temperature increase and volume expansion. A variety of coatings for percarbonate are described in the literature. Most of the coatings consist of inorganic substances such as borates [221, 222], perborax [223], sodium silicate [224, 196], sodium sulfate [225], and magnesium salts [226]. Mitsubishi describes a technology based on a two-layer coating with sodium silicate and a magnesium salt, which forms magnesium silicate on the surface of the granules [227]. Also organic coatings have been reported in the literature. Examples are chelating agents [228], fatty acids [229], and organic polymers [230, 231]. To control the liberation of hydrogen peroxide from sodium carbonate peroxohydrate Degussa developed a coating consisting of two layers: an inner layer of sodium sulfate for stability and an outer

layer of waterglass for time-delayed release [232].

The degrees of inner and outer stability of sodium carbonate peroxohydrate can both be checked by measuring the microcalorimetric properties of the materials by TAM. Sodium carbonate peroxohydrate qualities with 40 °C TAM values of less than 10 μ W/g after 48 h are considered to be stable during transportation, storage, and production, assuming proper handling of the material.

Sodium percarbonate must be stored under cool, dry conditions. Exothermic decomposition with liberation of oxygen can be accelerated by increased temperature, radiation caused by sunlight or steam piping, moisture, and/or contact with decomposition catalysts, e.g., heavy metals, alkali, or dirt. Adiabatic storage conditions can lead to self-accelerating decomposition. Exothermic decomposition may also occur during the manufacturing of detergents when sodium percarbonate is added to the still-warm base powder or when exothermic reactions, such as the rehydration of phosphates, proceed after the addition of sodium percarbonate.

Bulk storage of sodium percarbonate is more critical than storage of sodium perborates, in particular under hot and humid climatic conditions, due to its higher sensitivity to decomposition and caking.

Sodium percarbonate has been assigned recently to transport classification 5.1, oxidizing substances, by all major producers due to a change in the testing methods for oxidizing substances [59].

Sodium percarbonate is supplied in bulk by rail and truck, in big bags, and in 25 kg polyethylene sacks.

7.1.4. Uses

With the shift from sodium perborate to sodium carbonate peroxohydrate due to the ongoing discussion about the ecotoxicological properties of sodium perborate at the end of the 20th century, the most important areas of applications in terms of volume are nowadays all-purpose detergent powders and tablets. In 2004 it was estimated that the worldwide production capacity for sodium carbonate peroxohydrate was several hundred thousand tonnes. A smaller amount

of ca. 10 % of sodium carbonate peroxohydrate is used in the growing market of automatic dishwashing detergents, especially tablets. Sodium carbonate peroxohydrate also experienced a revival as bleach additive, mainly as oxy products for stain removal and boosters for laundry and dishwashing detergents. In a niche application, sodium carbonate peroxohydrate plays an important role in denture cleaners, often in combination with peroxomonosulfates like Caroat.

Major producers are Solvay (UK, Germany, Italy, USA) Degussa (Germany, Italy), OCI (USA, Korea), Mitsubishi (Japan), Kemira (Sweden), FMC (Spain), JSC (Russia), Jinke (China) and Aktivsauerstoff Gesellschaft (Austria).

7.2. Urea Peroxohydrate

7.2.1. Properties

Urea peroxohydrate [124-43-6], $(\text{NH}_2)_2\text{CO} \cdot \text{H}_2\text{O}_2$, M_r 94.1, is a white, crystalline substance that melts with decomposition between 80 and 90 °C. At 20 °C, 100 cm³ water dissolves 80 g urea peroxohydrate. The pH of aqueous percarbamid solution is 3.5–4.0. Urea peroxohydrate also exhibits good solubility in organic solvents, such as methanol (260 g/L), ethanol (120 g/L), glycerol (440 g/L), and various glycols. The bulk density is ca. 600 g/L.

The hydrogen peroxide content of the commercial products as powder is min. 35.0 wt %, and 33.4 wt % as tablets. The active oxygen content of these products is 16.5 and 15.7 wt %, respectively. When stored under cool and dry conditions, the active oxygen loss is less than 5 % per year. However, it decomposes on heating to form H_2O_2 , NH_3 , and CO_2 . The H_2O_2 is released first with vigorous decomposition, especially in the presence of water [233].

7.2.2. Production

Urea peroxohydrate was first synthesized by TANATAR in 1908 by mixing 30 % H_2O_2 with an aqueous solution of urea. After concentrating the reaction mixture, the product was precipitated by cooling and separated by filtration.

The modern industrial process is based on the same principal. Powdered urea is dissolved

in 35 % H_2O_2 in the presence of stabilizers, and the product is crystallized by cooling and concentration [234]. The precipitated solid material is separated from the mother liquor and dried at 30–40 °C. The mother liquor is further concentrated under vacuum and recycled. Alternatively, hydrogen peroxide can be sprayed onto urea in a fluidized bed. Excess moisture is removed by drying under vacuum at 30–40 °C [235].

7.2.3. Stabilization and Packaging

Urea peroxohydrate tends to decompose at elevated temperatures. The shelf life of the product can be improved by adding stabilizers such as NaH_2PO_4 or $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ [236].

The product is supplied commercially in 25 kg packages as powder or tablets. Suitable packaging materials are polyethylene bags or polyethylene-lined containers.

7.2.4. Uses

Urea peroxide is mainly used in the cosmetics and pharmaceutical industry as a disinfecting and bleaching agent. Percarbamide has been employed as the active ingredient in tooth whiteners and dentifrice formulations [237–240] which are sold in the United States as over-the-counter drugs. Worldwide consumption amounts to several hundred tonnes. The major producer of urea peroxide is Degussa (Germany).

8. Toxicology and Ecotoxicology

Metal peroxides, hydroperoxides, and ozonides cannot reasonably be tested for their toxicological and ecotoxicological properties due to their high reactivity to water with formation of oxygen and metal hydroxide or reaction with carbon dioxide to give metal carbonates. The toxicity is mediated by the high corrosivity to skin and mucous membranes of concentrated hydroxide solutions. Additionally, after direct contact with metal peroxides thermal burns can be developed due to the highly exothermic reaction with water.

Table 2. Acute toxicity data for peroxo compounds

Substance	LD ₅₀ (rat, oral), mg/kg	LD ₅₀ (dermal), mg/kg	LC ₅₀ (rat, inhalation), mg/m ³
Ammonium peroxodisulfate	495 ^a –742 ^c [241], [242]	> 2000 (rat) [242] ^b	> 2950 (4 h) [242]
Sodium peroxodisulfate	895 [245], [242]	> 10 000 (rabbit) [242] ^b	> 5100 [242] ^{c, d}
Potassium peroxodisulfate	1130 ^k [242]	10 000 (rabbit) [242]	42 900 (1 h) [242]
Potassium peroxomono sulfate triple salt	1204 [247]	> 2000 (rat) [248] ^b	> 5000 (4 h) [249] ^{cd}
Sodium percarbonate	1034 [250]	> 2000 (rat) [251] ^b	> 4580 (1 h) [252] ^{cd}
Sodium perborate monohydrate	1800	2000 (rabbit) [255][2]b	
Sodium perborate tetrahydrate	2243 [253]		1164 ^f [254]

^aFemale.^bLimit test.^cNo mortality occurred.^dMaximum concentration technically obtainable.^eMale.^fFor respirable particles [$< 10 \mu\text{m}$ mass medium aerodynamic diameter (MMAD)], lethality due to local irritant effects in the respiratory tract.

8.1. Toxicology

Most inorganic peroxo compounds are expected to have a similar toxicity profile to hydrogen peroxide as they release hydrogen peroxide on contact with water, with the exception of the peroxodisulfates.

Available acute toxicity data of the peroxo compounds are summarized in Table 2. All substances tested are of low toxicity by the dermal route and of low to moderate toxicity after oral administration or inhalation exposure. The effects observed are characterized by irritation and inflammation of the skin and mucous membranes at the site of application.

The results of skin and eye irritation and skin sensitization studies are summarized in Table 3. Most of the compounds, except potassium peroxomonosulfate triple salt, which is corrosive, are nonirritating or only slightly irritating to skin,

whereas eye irritation was evident for most of the substances. Some compounds cause irreversible corneal damage to the eye. Skin sensitization has only been reported for the peroxodisulfates. In humans, irritative and contact dermatitis but also asthmalike symptoms after exposure to higher airborne concentrations ($> 1 \text{ mg/m}^3$) have been reported with peroxodisulfates [269, 270]. These effects are possibly related to a direct histamine-liberating activity of peroxodisulfates. Sensory irritation studies in mice with sodium peroxodisulfate and sodium percarbonate resulted in RD₅₀ concentrations (concentrations that resulted in a 50 % depression of the respiratory rate) of 2250 mg/m³ [242] and 700 mg/m³ [271], respectively.

After repeated exposure to inorganic peroxo compounds, toxic effects are normally limited to irritative and inflammatory changes at the site of contact. After repeated inhalation exposure of rats with ammonium peroxodisulfate aerosol

Table 3. Experimental findings on irritation and skin sensitization by peroxo compounds

Substance	Skin irritation (rabbit)	Eye irritation (rabbit)	Skin sensitization (guinea pig)
Ammonium peroxodisulfate	not irritating [256]	slightly irritating [257]	sensitizing (optimization test) [258]
Sodium peroxodisulfate	not irritating [259]	not irritating [242]	sensitizing (optimization test) [260], not sensitizing (Buehler Test) [242]
Potassium peroxodisulfate	not irritating [242]	not irritating [242]	
Potassium bis(peroxomonosulfate) bis sulfate (Caroat)	corrosive [261]	highly irritating/corrosive [262]	not sensitizing (maximization test) [263]
Sodium percarbonate	slightly irritating [264]	highly irritating/corrosive [265]	not sensitizing (Bühler Test) [266]
Sodium perborate monohydrate	slightly irritating [254]	highly irritating/corrosive [254]	not sensitizing (Bühler Test) [268]
Sodium perborate tetrahydrate	not irritating [267]	irritating [267]	

(1–20 mg/m³, 23.5 h/d, 7 d) effects indicative of irritation and inflammation of the respiratory tract including the lung were observed; the no observed adverse effect level (NOAEL) was 1 mg/m³ [272]. A 90-d inhalation study in rats exposed 6 h per day for 5 d per week to concentrations of 5, 10, or 25 mg/m³ of ammonium peroxodisulfate revealed an NOAEL of 10 mg/m³, with the only effects being local irritation of trachea, bronchi/bronchioles, and lungs. In this study a NOEL of 5 mg/m³ was identified based on sporadic rale and effects on the respiratory rate in the 10 mg/m³ dose group. All effects were reversible during a 6-week recovery period. No systemic effects or histopathological changes in any organs distant from the site of first contact were observed [242]. Rats exposed to concentrations of 1.4–43 mg/m³ of potassium bis(peroxomonosulfate) bis-sulfate dust by inhalation for 6 h/d, 5 d per week for 2 weeks showed severe ocular irritation as the main effect (NOAEL 1.4 mg/m³); no pathological changes in other organs were observed [275].

No effects were observed in male rats receiving up to 1000 ppm sodium peroxodisulfate or potassium peroxodisulfate in the diet (corresponding to 137 mg/kg bw or 131.5 mg/kg bw, respectively) for 28 d [242]. In a 28-d feeding study in male rats with ammonium peroxodisulfate an NOAEL of 300 ppm in the diet, corresponding to 41 mg/kg bw was identified based on a decreased adrenal weight to body weight ratio at 82 mg/kg bw [242]. In a 13-week feeding study in rats with 3000 ppm sodium peroxodisulfate in the diet (corresponding to 300 mg/kg bw) local effects on the mucous membranes of the gastrointestinal tract were found, but no systemic toxicity was observed. The NOAEL in this study was 300 ppm or 30 mg/kg bw [269, 270]. In a 28-d study in rats receiving 1000 mg/kg bw of sodium perborate tetrahydrate by gavage, similarly the observed effects could be related to irritation of the mucous membranes in the gastrointestinal tract [276].

The effects observed are consistent with the liberation of hydrogen peroxide by the peroxo compounds, which showed similar effects after repeated oral administration. In a 90-d drinking water study in mice receiving 100 to 3000 ppm of hydrogen peroxide, irritation of the mucous membranes of the gastrointestinal tract was observed (the NOAEL was 100 ppm,

corresponding to 26 or 37 mg/kg/day for male and female mice, respectively). No systemic effects were observed [274]. Hydrogen peroxide is rapidly degraded in the exposed tissues and blood, catalyzed by metabolic enzymes such as catalases or peroxidases. Therefore systemic availability of peroxo compounds and hydrogen peroxide is thought to be low [273].

Ammonium and sodium peroxodisulfates were nonmutagenic in a variety of *in vitro* and *in vivo* test systems for point mutations and chromosomal aberrations with and without a metabolic activation system [242, 269, 277–280] and potassium bis(peroxomonosulfate) bis-sulfate was nonmutagenic in the Ames assay [281].

Results of mutagenicity studies with sodium perborate were comparable to those with hydrogen peroxide [273], [282–285].

While *in vitro* assays for gene mutation and chromosomal aberration were positive in the absence of a metabolic system (rat liver supernatant, catalase), the mutagenic activity was reduced or abolished when an exogenic metabolic system was added [273], [282], [283]. No *in vivo* data for sodium perborate are available, but hydrogen peroxide was nonmutagenic with regard to chromosomal aberrations or micronuclei in rats and mice as well as in a study for unscheduled DNA synthesis in rats [273], [284].

No carcinogenicity studies are available for peroxo compounds, but the carcinogenic effects of hydrogen peroxide were studied in rats and different strains of mice after oral administration. [272–288]. Available evidence suggests that hydrogen peroxide and peroxo compounds are not likely to cause cancer in humans except by uncommon or unlikely routes of exposure [289].

No effects on male and female fertility were observed in a one-generation study in rats with ammonium peroxodisulfate up to the highest tested dose level of 250 mg (kg bw)⁻¹d⁻¹ in the diet. No effects on embryo/fetal viability up to day 4 of lactation were observed in the same study. The NOAEL for both fertility and developmental toxicity was 250 mg (kg bw)⁻¹d⁻¹ [242].

A potential for systemic toxicity of sodium perborates could be the formation of boric acid. However the uptake of boric acid in the body is limited by the simultaneous liberation of hydrogen peroxide that reduces local blood circulation.

Table 4. Ecotoxicity data of peroxo compounds

Substance	Acute toxicity for fish LC ₅₀ , 96-h (mg/L)	Acute toxicity for daphnia EC ₅₀ , 48-h (mg/L)	Chronic toxicity for algae EC ₅₀ , 72-h (mg/L)
Ammonium peroxodisulfate	<i>Oncorhynchus mykiss</i> 76.3 [295]	<i>Daphnia magna</i> 120 [298]	<i>Scenedesmus quadricauda</i> 33 ^a (growth rate) [300] <i>Selenastrum capricornutum</i> (growth rate): 83.7 [242] <i>Selenastrum capricornutum</i> (bio- mass): 116 [242]
Sodium peroxodisulfate	<i>Oncorhynchus mykiss</i> 163 [242]	<i>Daphnia magna</i> 133 [299]	
Potassium peroxomonosulfate triple salt	<i>Brachydanio rerio</i> > 32 < 56 [301]	<i>Daphnia magna</i> 5.3 ^b [303]	
Sodium percarbonate	<i>Pimephales promelas</i> 71 [302]	<i>Daphnia pulex</i> 4.9 [304]	<i>Anabaena spec</i> (blue-green) 8 ^c [305] <i>Chlamydomonas spec</i> (green) 60 ^d [305]
Sodium perborate monohydrate	<i>Brachydanio rerio</i> 51 [306]	<i>Daphnia magna</i> 11 [307]	<i>Selenastrum capricornutum</i> 3.3 (biomass) [308] 6.3 (growth rate) [308]

^a EC₁₀ (96-h).^b 24-h.^c 140-h.^d 240-h.

After repeated oral administration of high doses of boric acid to experimental animals, effects on male fertility (testicular atrophy) and developmental toxicity were observed [290]. For sodium perborate there is no indication of any effect on reproductive organs in a repeated dose study by the oral route (28 d, 7 d per week at 1000 mg (kg bw)⁻¹d⁻¹) in rats at dose levels corresponding to boron doses that already revealed considerable testicular toxicity in studies with boric acid. As these perborate doses corresponded to the maximum tolerated dose in the animals, it can be concluded that sodium perborate did not cause any testicular effect in rats at the maximum tolerated dose of 1000 mg (kg bw)⁻¹d⁻¹ [254]. In a developmental toxicity study by the oral route in rats with sodium perborate tetrahydrate, fetotoxic effects were only observed at dose levels that were already maternally toxic [254].

No occupational exposure limits exist for perborates, sodium percarbonate, and peroxomonosulfate. Occupational exposure limits have been established for hydrogen peroxide in different countries, for example, by ACGIH [288], the Dutch Social Economic Council [290], the UK Health and Safety Executive (HSE) [291], Belgium [292], the French Ministry of Labour [293], and the German AGS (Ausschuss für Gefahrstoffe) [294]: 8-h TWA: 1.4 mg/m³ or 1.5 mg/m³. A 15-min STEL of 2.8 mg/m³ was established by HSE (max. 1 h in a 24 h period)

[294], and a 15-min. STEL of 1.4 mg/m³ by AGS [294].

For peroxodisulfates occupational exposure limits have been established by ACGIH (8-h TWA: 0.1 mg/m³ [288]), the UK HSE, and Belgium (8-h TWA: 1 mg/m³ [291], [292]).

8.2. Ecotoxicology

Ecotoxicological data are available for a number of peroxo compounds. The data are summarized in Table 4.

Peroxodisulfates are of low to moderate toxicity to aquatic organisms in standard tests [295–300].

Potassium peroxomonosulfate triple salt and sodium percarbonate exhibit moderate toxicity to fish, daphnia, and algae [301–305].

Sodium perborate monohydrate is of moderate toxicity to fish, daphnia, and algae [306–308]. Algae seem to be the most sensitive phylum.

Peroxo compounds tend to decompose in natural waters to give hydrogen peroxide and ultimately oxygen and water. In wastewater peroxide was shown to decompose before reaching the sewage treatment plant [309]. Therefore it is expected that peroxo compounds do not persist long enough in water to cause an impact on the environment in low concentrations. Given the polarity and high water solubility of peroxo

compounds, a potential for bioaccumulation is not anticipated.

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