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SODIUM NITRITE

Sodium nitrite [7362-00-0], $NaNO_2$, a stable, odorless, pale yellow or straw-colored compound of molecular weight 69.00, is the sodium salt of nitrous acid [7782-77-6], HNO_2. Sodium nitrite has been produced commercially in the United States since the 1920s, and is available in dry granular or flake forms, as well as in water solutions. Most of the common package types are offered, from bags to drums to bulk. Sodium nitrite is used in dye, rubber chemicals and pharmaceuticals manufacture, as a corrosion inhibitor, in heat treating and heat-transfer salts, in meat curing, and several other applications. The U.S. market is served primarily by domestic producers, with some imports. Production is by absorption of oxides of nitrogen into sodium carbonate or sodium hydroxide solutions. Sodium nitrite is an oxidizer and is toxic; as such, it requires care in its handling, storage, and use.

1. Properties

Pure anhydrous crystalline sodium nitrite has a specific gravity of 2.168 at 0°C/0°C (1). The crystal structure is body-centered orthorhombic, having the unit cell dimensions $a = 0.355$ nm, $b = 0.556$ nm, and $c = 0.557$ nm (2). Sodium nitrite melts at ∼284°C and decomposition begins above 320°C, yielding N_2, O_2, NO, and Na_2O. The heat of formation is −362.3 kJ/mol (−86.6 kcal/mol) at 25°C (3). Sodium nitrite has a transition point at 158–165°C and displays significant changes in physical properties within this temperature range. The specific heat increases gradually from ∼980 J/(kg·K) (0.234 cal/(g°C)) at 60°C to ∼1160 J/(kg·K) (0.277 cal/(g°C)) at 200°C, but exhibits a peak value of ∼2290 J/(kg·K) (0.547 cal/(g°C)) at 161°C corresponding to this transition temperature (1).

Sodium nitrite is hygroscopic and very soluble in water. Dissolution of sodium nitrite in water results in the absorption of heat in the amount of 15.1 kJ/mol (3.6 kcal/mol) at 18°C (3). Water solubility characteristics are displayed in Figure 1. Sodium nitrite has limited solubility in most organic solvents (Table 1). The pH of a 1% solution of sodium nitrite is ∼9. A hemihydrate, $NaNO_2 \cdot 1/2H_2O$ [82010-95-5], reported at temperatures below −5.1°C, is of no known commercial significance. The eutectic composition is 28.1% $NaNO_2$, although some supercooling of solutions up to ∼38% may occur.

Sodium nitrite is stable in alkaline solutions. Acidification liberates nitrous acid which is unstable. The decomposition of nitrous acid yields nitric acid [7697-37-2], HNO_3, according to the following reaction:

$$3\ HNO_2\ (aq) \longrightarrow HNO_3\ (aq) + 2\ NO\ (g) + H_2O$$

Colorless nitric oxide [10102-43-9], NO, spontaneously oxidizes, in the presence of atmospheric oxygen, to brown-colored nitrogen dioxide [10102-44-0], NO_2. The resulting mixture of NO and NO_2, commonly referred to as NO_x gases, is corrosive and toxic and its generation should be avoided. Nitrous acid is not an article of commerce owing to its inherent instability. Sodium nitrite serves as the primary industrial source for nitrous

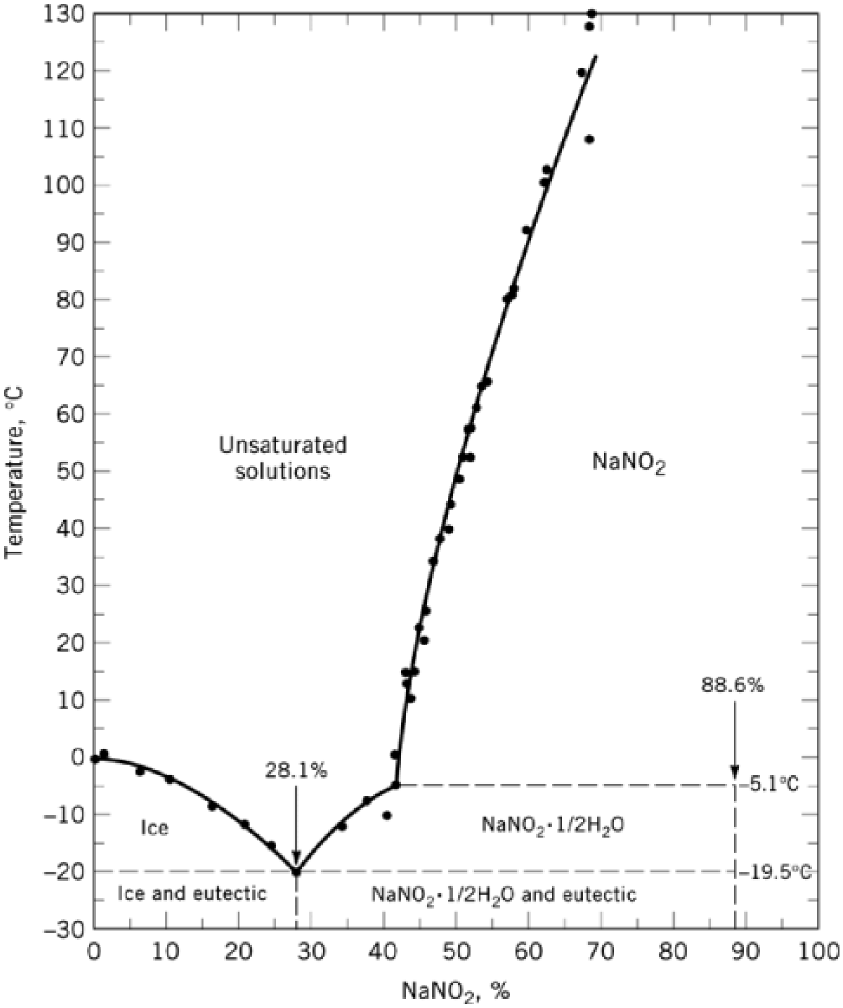

Fig. 1. Sodium nitrite solubility in water where (_) represents solid-phase boundaries (1, 2, 4, 5).

acid in organic syntheses, for instance in the diatozation and nitrosation of aromatic amines. Under controlled conditions of acidification, the nitrous acid generated can react before excessive decomposition occurs.

As an oxidizer, sodium nitrite can convert ammonium ion to nitrogen, urea to carbon dioxide and nitrogen, and sulfamate to sulfate and nitrogen. The oxidizing properties of sodium nitrite contribute to its application as a corrosion inhibitor (see Corrosion and corrosion control), in detinning of scrap tinplate, and phosphating of metal surfaces. Because it is a strong oxidizer, sodium nitrite is capable of supplying oxygen and thus accelerating the combustion of organic matter. It can undergo vigorous, perhaps violent reactions with certain inorganic compounds such as ammonium salts, acidic materials, thiocyanates, and thiosulfates. It functions as a reducing agent to more powerful oxidizers such as dichromate, permanganate, chlorate, and chlorine. At ambient temperatures, sodium nitrite is stable; it slowly oxidizes to sodium nitrate at elevated temperatures (see Sodium compounds, sodium nitrate). References 1 and 2 provide comprehensive data on the physical and chemical properties of sodium nitrite.

Table 1. Solubility of Sodium Nitrite in Nonaqueous Solvents[a]

Solvent	g $NaNO_2$/100 g solvent	Temperature, °C
acetone	insoluble	
ammonia, anhydrous	very soluble	−77 to 172
ethanol		
absolute	0.31	19.5
94.9%	1.424	25
ethylenediamine	12.60	30
ethylene glycol	16.78	25
methanol, absolute	4.43	19.5
methyl ethyl ketone	insoluble	
monoethanolamine	8.74	30
propylene glycol	8.47	25
pryridine	0.34	25

[a] Refs. 4 and 6.

2. Manufacturing

Sodium nitrite has been synthesized by a number of chemical reactions involving the reduction of sodium nitrate [7631-99-4], $NaNO_3$. These include exposure to heat, light, and ionizing radiation (2), addition of lead metal to fused sodium nitrate at 400–450°C (2), reaction of the nitrate in the presence of sodium ferrate and nitric oxide at ~400°C (2), contacting molten sodium nitrate with hydrogen (7), and electrolytic reduction of sodium nitrate in a cell having a cation-exchange membrane, rhodium-plated titanium anode, and lead cathode (8).

Industrial production of sodium nitrite is by absorption of nitrogen oxides (NO_x) into aqueous sodium carbonate or sodium hydroxide. NO_x gases originate from catalytic air oxidation of anhydrous ammonia, a practice common to nitric acid plants:

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O$$

Gas contact is typically carried out in absorption towers over which the alkaline solutions are recirculated. Strict control over the conditions of absorption are required to efficiently capture the NO_x and convert it predominantly to sodium nitrite according to the following reaction, thereby minimizing the formation of by-product sodium nitrate. Excessive amounts of nitrate can impede the separation of pure sodium nitrite from the process.

$$2\ NaOH + NO + NO_2 \longrightarrow 2\ NaNO_2 + H_2O$$

Solutions of sodium nitrite thus produced are concentrated and a slurry of crystals obtained in conventional evaporation (qv) and crystallization (qv) equipment. Much of this equipment can be of mild steel construction because sodium nitrite functions as a corrosion inhibitor toward most ferrous metals. The crystals are typically separated from the mother liquor by centrifugation and subsequently dried. Because of its tendency to lump and cake rapidly in storage, dry sodium nitrite products are frequently treated with an anticaking agent to keep them free-flowing. Alternatively, larger flakes or pellets are prepared from the granular material through a compaction process. The limited surface contact between these larger particles allows them to remain uncaked for extended periods. Technical solutions for commerce can be obtained directly from the process; higher purity solution products are prepared by dissolving crystals.

3. Shipment and Storage

Dry products of sodium nitrite are most commonly packaged into 22.7 kg (50 lb) or 45.4 kg (100 lb) multi-ply paper bags which contain a polyethylene moisture barrier. Fiber drums and semibulk sacks are also utilized. Bulk shipments are limited to flake material in specially designed sparger cars which allow the material to be unloaded as a solution. Dry sodium nitrite is regulated by the U.S. Department of Transportation (DOT) and classified as an Oxidizer, Hazard Class 5.1, UN1500, UN Packaging Group III (9). Containers must bear the Class 5.1 Oxidizer label, and bulk shipments must be placarded appropriately.

Liquid sodium nitrite products are typically 40–42% $NaNO_2$ and can be shipped in tank cars or tank trucks when volume and freight considerations allow. Sodium nitrite solutions are also regulated by the DOT and classified as Nitrites, Inorganic, Aqueous Solution, NOS, Hazard Class 5.1 Oxidizer, UN3219, UN Packaging Group III (9). Liquid product must also carry the Oxidizer label. Lesser quantities of liquid product may also be available in drums from local chemical distributors. Solution products are often preferred because of more convenient, efficient, and cost-effective handling versus bagged material and compatibility with inexpensive mild steel equipment.

Care must be exercised in using sodium nitrite near other chemicals. It is incompatible with ammonium salts, thiocyanates, thiosulfates, and strong reducing agents. In acid solutions, sodium nitrite evolves toxic NO_x; in the presence of secondary amines it can form nitrosamines which are suspected carcinogens.

Sodium nitrite exhibits good shelf-life characteristics if stored in secure containers in a cool, dry place, segregated from combustible and incompatible materials. Sodium nitrite does not burn, but its decomposition in fire promotes burning by furnishing additional oxygen. In the case of fire, water flooding should be used and the runoff kept away from streams and sewers to the extent possible. If spilled, care should be exercised to avoid contact with any acidic materials, as toxic NO_x could evolve. Under current regulations, spills in excess of 45.4 kg (100 lb) of dry sodium nitrite equivalent are reportable to the U.S. EPA (10). Additional state and/or local regulations may also apply.

4. Health and Safety Factors

Sodium nitrite is poisonous and prolonged contact with dry sodium nitrite or its solutions can cause irritation to the skin, eyes, and mucous membranes. The LD_{50} (oral, rat) is 85 mg per kg body weight (11). Inhalation or ingestion of significant quantities of dust or mist may result in acute toxic effects such as nausea, cyanosis, and low blood pressure, which can lead to possible collapse, coma, and even death.

Persons responsible for the procurement, use, or disposal of sodium nitrite products should become familiar with safety information contained in the manufacturer's Product Safety Data Sheet (PSDS) (12). For handling dry products, a hard hat, safety glasses, impervious gloves, and long sleeves should be worn as a minimum. Where dusty or misty conditions prevail or when handling solutions, a NIOSH-approved respirator, chemical goggles, and full impervious clothing may be required. Contact lenses should not be worn. Persons should wash thoroughly after handling sodium nitrite. Eating or smoking in areas where sodium nitrite is being handled should be prohibited.

In case of skin contact, the area should be washed thoroughly with water and examined by a physician if irritation persists. If exposed, the eyes should be flushed with water for at least 15 minutes. Remove inhalation victims to fresh air and administer artificial respiration if the victim is not breathing. If ingested, vomiting should be induced. All incidents should be followed by prompt medical attention.

Table 2. Specifications for Dry Grades of Sodium Nitrite

Parameter[a]	Technical[b]	USP[c]	Food[d]	Reagent[e]
assay, as $NaNO_2$, wt %[f]	97.0	97.0–101.0	97.0	97.0
loss on drying, wt %[f]		0.25	0.25	
heavy metals, as Pb, %		0.002	0.002	0.001
arsenic, as As, ppm			3	
lead, as Pb, ppm			10	
sodium sulfate, as Na_2SO_4, wt %	0.2			
sodium chloride, as NaCl, wt %	0.2			
insolubles, wt %	0.5			0.01
pH	8 ± 1			
chloride, as Cl, wt %				0.005
sulfate, as SO_4, wt %				0.01
calcium, as Ca, wt %				0.01
iron, as Fe, wt %				0.001
potassium, as K, wt %				0.005

[a] Value is maximum unless noted.
[b] Ref. 14.
[c] Ref. 15.
[d] Ref. 16.
[e] Ref. 17.
[f] Value is minimum.

5. Specifications, Analysis, and Quality

Dry sodium nitrite is offered in several grades: technical, drug (*U.S. Pharmacopeia* (USP)), food (*Food Chemicals Codex* (FCC)), and reagent (American Chemical Society (ACS)). Granular product has a tendency to lump and cake into an unmanageable mass during storage. Flake or treated granular types overcome this caking tendency and exhibit excellent shelf life. The most commonly used anticake is sodium mono- and dimethyl naphthalene sulfonates at a typical dosage of $\leq 0.1\%$. This is the only such agent allowed in the food-grade product in the United States (13). The USP and reagent ACS grades contain no anticake, and in granular form harden within weeks. Dry products typically contain $>99\%$ sodium nitrite and $<1\%$ sodium nitrate; a small amount of residual alkalinity is also present. The specifications for technical, USP, food, and ACS reagent grades are given in Table 2. Typically liquid products are of a technical or purified grade containing between 35 and 45% sodium nitrite and varying levels of nitrate.

Sodium nitrite products can be analyzed using methods that accompany specifications for the particular grade of product used. Assay methods are typically based on oxidation of the sample by a known excess of standard potassium permanganate solution, which is in turn reduced with a known excess of standard oxalic acid or ferrous ammonium sulfate solution. The excess is then titrated to a pink color end point and calculation gives the percent sodium nitrite in the sample. Standard laboratory analytical equipment such as hot plates, glassware, reagents, and analytical balances are required to run the tests. Careful attention to the standardization of reagents is important in obtaining reliable results. In contaminated or process samples, other substances present, which may be oxidized by potassium permanganate, give positive interferences. The analysis should be carried out in a proper fume hood to avoid the introduction of toxic gases into the workplace. The same safety precautions apply to handling sodium nitrite in the laboratory as previously described for the production area. Complete details on assay procedures and impurities testing are available (4, 14–17).

Nitrite can be estimated in the field by using one of the many available test kits offered by a number of companies specializing in this area including Chemetrics, Inc. (Calverton, Virginia) and the Hach Company

(Loveland, Colorado). These kits are designed for specific concentration ranges, involve simple procedures, and provide accuracy reasonable for field work by using color comparators or by counting drops of titrant to a color-change end point. Facilities producing the drug and food grades must follow a rigid set of guidelines for cleanliness and product reliability known as Good Manufacturing Practices (GMPs) and avail their plants to inspections by the U.S. FDA. Accurate and thorough recordkeeping is also required in the production of these grades. General Chemical Corporation's sodium nitrite facility has had its quality system registered (October 1993) as complying with the internationally recognized quality standard ISO 9002.

6. Uses

The many industrial uses for sodium nitrite primarily are based on its oxidizing properties or its liberation of nitrous acid in acidic solutions.

6.1. Dyes

Sodium nitrite is a convenient source of nitrous acid in the nitrosation and diatozation of aromatic amines. When primary aromatic amines react with nitrous acid, the intermediate diamine salts are produced which, on coupling to amines, phenols, naphthols, and other compounds, form the important azo dyes (qv). The color center of the dye or pigment is the $-N{=}N-$ group and attached groups modify the color. Many dyes and pigments (qv) have been manufactured with shades of the entire color spectrum.

6.2. Rubber Chemicals

Sodium nitrite is an important raw material in the manufacture of rubber processing chemicals. Accelerators, retarders, antioxidants (qv), and antiozonants (qv) are the types of compounds made using sodium nitrite. Accelerators, eg, thiuram [137-26-8], greatly increase the rate of vulcanization and lead to marked improvement in rubber quality. Retarders, on the other hand (eg, *N*-nitrosodiphenylamine [156-10-5]), delay the onset of vulcanization but do not inhibit the subsequent process rate. Antioxidants and antiozonants, sometimes referred to as antidegradants, serve to slow the rate of oxidation by acting as chain stoppers, transfer agents, and peroxide decomposers. A commonly used antioxidant is N,N'-disubstituted *p*-phenylenediamine which can employ sodium nitrite in its manufacture (see Rubber chemicals).

6.3. Heat Treatment and Heat-Transfer Salts

Mixtures of sodium nitrite, sodium nitrate, and potassium nitrate are used to prepare molten salt baths and heat-transfer media. One of the most widely used eutectic mixtures uses 40% $NaNO_2$, 7% $NaNO_3$, and 53% KNO_3 [7757-79-1] to give a melting point of 143°C. Its advantages are low melting point, high heat-transfer rate, thermal stability to 538°C, and a noncorrosive effect on steel (qv) at high temperature. The salts can be used for indirect heating or cooling or as quenching baths in the annealing of iron and steel.

6.4. Corrosion Inhibition

Sodium nitrite acts as an anodic inhibitor toward ferrous metals by forming a tightly adhering oxide film over the steel, preventing the dissolution of metal at anodic areas. When used in mixed metal systems that may include, for instance, copper, brass, or aluminum (as in automobile cooling systems), synergistic additives may be required for complete system protection. Some renewed interest in furthering nitrite use has been spawned from reduction in widespread use of carcinogenic hexavalent chromium-based inhibitors. Loss of protection owing to biological consumption of nitrite has been addressed by the use of higher initial concentrations (18). Sodium nitrite is used in boiler water treatment, as a dip or spray for protection of metals in process and storage, and in concrete. The EPA has ruled that sodium nitrite should not be used as a corrosion inhibitor in amine-based metalworking fluids because of the formation of potentially carcinogenic nitrosamines (19).

6.5. Metal Finishing

In phosphating solutions, sodium nitrite performs as an accelerator and oxidizer, serving to reduce processing times and control buildup of ferrous ions in solution, respectively. Phosphate coatings are applied to steel as a base coating before painting. In gold–sulfite-plating baths, sodium nitrite functions in the formation a gold–sulfite–nitrite complex. $Na_4Au(SO_3)_2NO_2$ [51846-25-4], from which the gold can be electrolytically deposited (20) (see Gold and gold compounds). This bath is considered to be safer than the poisonous cyanide baths traditionally used for gold plating. Sodium nitrite is also used in the recovery of tin from scrap tinplate (see Tin and tin alloys). It functions as an oxidizer in converting tin to sodium stannate with caustic soda; high purity tin can then be electroplated directly from the stannate solution.

6.6. Meat Curing

Sodium nitrite is used extensively in curing meat and meat products (qv), particularly pork products such as ham, bacon, frankfurters, etc. As an ingredient in curing brines, sodium nitrite acts as a color fixative and inhibits bacteria growth, including *Clostridium botulinum*, the source of the botulism toxin. Certain fish and poultry products are also cured with brines containing sodium nitrite. All food uses of sodium nitrite are strictly regulated by the FDA (21) and USDA.

6.7. Other Uses

Other applications for sodium nitrite include the syntheses of saccharin [81-07-2] (see Sweeteners), synthetic caffeine [58-08-2] (22), fluoroaromatics (23), and other pharmaceuticals (qv), pesticides (qv), and organic substances; as an inhibitor of polymerization (24); in the production of foam blowing agents (25); in removing H_2S from natural gas (26); in textile dyeing (see Textiles); as an analytical reagent; and as an antidote for cyanide poisoning (see Cyanides).

Sodium nitrite has played a key role in the invention of the following: a freezing point depressant in a large steel thermal storage tank for a district cooling system (27), antifungal agent for treatment of skin diseases (28); vapor-phase corrosion inhibitor–desiccant material (29); method for estimating methyl anthranilate [134-20-3] (30); process for preparing optically active benzoic acid (qv) derivatives (31); process for dewaxing oil-producing formations (32); method for treating chelated metal wastewaters (33); method of sewage sludge treatment (34); and preparation of iron nitrosyl carbonyl catalysts (35).

7. Economic Aspects

Sodium nitrite is manufactured in the United States by General Chemical Corporation at their plant in Solvay, New York, and by E. I. du Pont Company's Gibbstown, New Jersey plant. Recent U.S. demand is estimated to be between 50,000 and 60,000 metric tons per year, the vast majority of which is produced domestically. Imports primarily have been from Germany and Poland; lesser amounts originate from the United Kingdom, the Netherlands, and China. The quantity of product imported into the United States has varied in the 1990s from ∼1000 to 4000 t/yr. Currency exchange rates have had a decided influence on import volumes. The list price of sodium nitrite in 45.4 kg (100 lb) bags, fob works in August 1996, was reported to be \$0.907/kg (\$0.412/lb) versus \$0.66/kg (\$0.30/lb) in 1980, on the same basis. Liquid products sell at discounted equivalent-basis prices.

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Related Articles

Sodium nitrate; Sweeteners; Rubber chemicals