Bleach

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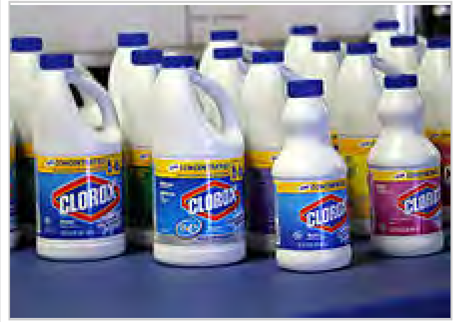
Bleach is a chemical that whitens clothing.



Clorox bleach

The bleaching process has been known for millennia,[1] but the chemicals currently used for bleaching resulted from the work of several 18th century scientists. Chlorine is the basis for the most common bleaches: for example, the solution of sodium hypochlorite, which is so ubiquitous that most simply call it "bleach", and calcium hypochlorite, the active compound in "bleaching powder". Oxidizing bleaching agents that do not contain chlorine are usually based on peroxides such as hydrogen peroxide, sodium percarbonate and sodium perborate. While most bleaches are oxidizing agents, some are reducing agents such as sodium dithionite and sodium borohydride.

Bleaches are used as household chemicals to whiten clothes and remove stains and as disinfectants, primarily in the bathroom and kitchen. Many bleaches have strong bactericidal properties, and are used for disinfecting and sterilizing and thus are used in swimming pool sanitation to control bacteria, viruses and algae and in any institution where sterile conditions are needed. They are also used in many industrial processes, notably in the bleaching of wood pulp. Bleach is also used for removing mildew, killing weeds and increasing the longevity of cut flowers.[2]

Contents

History

The earliest form of bleaching involved spreading fabrics and cloth out in a bleachfield to be whitened by the action of the sun and water.[1][3] Modern bleaches resulted from the work of 18th century scientists including Swedish chemist Carl Wilhelm Scheele, who discovered chlorine,[1] French scientists Claude Berthollet, who recognized that chlorine could be used to bleach fabrics[1] and who first made sodium hypochlorite (*Eau de Javel*, or Javel water, named after a quarter in Paris where it was produced) and Antoine Germain Labarraque, who discovered the disinfecting ability of hypochlorites. Scottish chemist and industrialist Charles Tennant first produced a solution of calcium hypochlorite, then solid calcium hypochlorite (bleaching powder).[1]

Louis Jacques Thénard first produced hydrogen peroxide in 1818 by reacting barium peroxide with nitric acid.[4] Hydrogen peroxide was first used for bleaching in 1882, but did not become commercially important until after 1930.[5] Sodium perborate as a laundry bleach had been used in Europe since the early twentieth century, but did not become popular in North America until the 1980s.[6]

Mechanism of action

Whitening

Colors typically arise from organic dye and pigments, such as beta carotene. Chemical bleaches work in one of two ways:

- An oxidizing bleach works by breaking the chemical bonds that make up the chromophore. This changes the molecule into a different substance that either does not contain a chromophore, or contains a chromophore that does not absorb visible light. This is the mechanism of bleaches based on chlorine.
- A reducing bleach works by converting double bonds in the chromophore into single bonds. This eliminates the ability of the chromophore to absorb visible light. This is the mechanism of bleaches based on sulfur dioxide.[7]

Sunlight acts as a bleach through a process leading to similar results: high energy photons of light, often in the violet or ultraviolet range, can disrupt the bonds in the chromophore, rendering the resulting substance colorless. Extended exposure often leads to massive discoloration usually reducing the colors to white and typically very faded blue spectrums.[8]

Antimicrobial efficacy

The broad-spectrum effectiveness of bleach, particularly sodium hypochlorite, is owed to the nature of its chemical reactivity with microbes. Rather than acting in an inhibitory or toxic fashion in the manner of antibiotics, bleach quickly reacts with microbial cells to irreversibly denature and destroy many pathogens. Bleach, particularly sodium hypochlorite, has been shown to react with a microbe's heat shock proteins, stimulating their role as intra-cellular chaperone and causing the bacteria to form into clumps (much like an egg that has been boiled) that will eventually die off.[9] In some cases, bleach's base acidity compromises a bacterium's lipid membrane, a reaction similar to popping a balloon. The range of micro-organisms effectively killed by bleach (particularly sodium hypochlorite) is extensive, making it an extremely versatile disinfectant. The same study found that at low (micromolar) sodium hypochlorite levels, *E. coli* and *Vibrio cholerae* activate a defense mechanism that helps protect the bacteria, though the implications of this defense mechanism have not been fully investigated.[9]

In response to infection, the human immune system will produce a strong oxidizer, hypochlorous acid, which is generated in activated neutrophils by myeloperoxidase-mediated peroxidation of chloride ions, and contributes to the destruction of bacteria.[10][11][12]

Classes of bleaches

Chlorine-based bleaches

Chlorine-based bleaches are found in many household cleaners. The concentration of chlorine-based bleaches is often expressed as percent active chlorine where one gram of a 100% active chlorine bleach has the same bleaching power as one gram of chlorine. These bleaches can react with other common household chemicals like vinegar or ammonia to produce toxic gases. Labels on sodium hypochlorite bleach warn about these interactions.

Chemical interactions

Mixing a hypochlorite bleach with an acid can liberate chlorine gas. Hypochlorite and chlorine are in equilibrium in water; the position of the equilibrium is pH dependent and low pH (acidic) favors chlorine,[13]

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HClO$$

Chlorine is a respiratory irritant that attacks mucous membranes and burns the skin. As little as 3.53 ppm can be detected as an odor, and 1000 ppm is likely to be fatal after a few deep breaths. Exposure to chlorine has been limited to 0.5 ppm (8-hour time-weighted average—38-hour week) by OSHA in the U.S.[14]

Sodium hypochlorite and ammonia react to form a number of products, depending on the temperature, concentration, and how they are mixed.[15] The main reaction is chlorination of ammonia, first giving chloramine (NH_2Cl), then dichloramine ($NHCl_2$) and finally nitrogen trichloride (NCl_3). These materials are very irritating to the eyes and lungs and are toxic above certain concentrations; nitrogen trichloride is also a very sensitive explosive.

$$NH_3 + NaOCl \rightarrow NaOH + NH_2Cl$$

$$NH_2Cl + NaOCl \rightarrow NaOH + NHCl_2$$

$$NHCl_2 + NaOCl \rightarrow NaOH + NCl_3$$

Additional reactions produce hydrazine, in a variation of the Olin Raschig process.

$$NH_3 + NH_2Cl + NaOH \rightarrow N_2H_4 + NaCl + H_2O$$

The hydrazine generated can react with more chloramine in an exothermic reaction to produce ammonium chloride and nitrogen gas:[13]

$$2\ NH_2Cl + N_2H_4 \rightarrow 2\ NH_4Cl + N_2$$

However, the place of atomic oxygen in accounting for the formation of chlorine is not as plausible as another theory based on the so-called 'chloride system' employed in modern hydrometallurgy to dissolve ores with weak acids in highly ionic and concentrated salt solutions. Salts particularly effective, in this regard, include $MgCl_2$, $CaCl_2$, $FeCl_3$ and, to a lesser extent, the mono-valent NaCl. This is, in effect, an application of the non-common ion theory, or as discussed in Wikipedia under Solubility Equilibrium as the 'salt effect'. With respect to bleaching powder, which has been described as a compound salt of the form $Ca(ClO)_2.CaCl_2.Ca(OH)_2.xH_2O$, the presence of $CaCl_2$ in very concentrated solutions can greatly increase the 'activity level' of weak acids. So, in this particular proposed application, H_2CO3 from CO_2 and moisture on the bleaching powder, acts on the $CaCl_2$ to release some HCl which acts on the HClO releasing Chlorine:

$$HClO + HCl \rightarrow H_2O + Cl_2$$

or, the increasing acidity creates more HClO which moves the following known (and old, see Watt's Dictionary of Chemistry) equilibrium reaction to the right:

$$CaCl_2 + 2\ HClO = Ca(OH)_2 + 2\ Cl_2$$

Sodium hypochlorite

Sodium hypochlorite is the most commonly encountered bleaching agent, usually as a dilute (3–6%) solution in water. This solution of sodium hypochlorite, commonly referred to as simply "bleach", was also one of the first mass-produced bleaches. It is produced by passing chlorine gas through a dilute sodium hydroxide solution[16]

$$Cl_2\ (g) + 2\ NaOH\ (aq) \rightarrow NaCl\ (aq) + NaClO\ (aq) + H_2O\ (l)$$

or by electrolysis of brine (sodium chloride in water).[16][17]

$$2\ Cl^- \rightarrow Cl_2 + 2\ e^-$$
$$Cl_2 + H_2O \leftrightarrow HClO + Cl^- + H^+$$

The dilute solution of sodium hypochlorite is used in many households to whiten laundry, disinfect hard surfaces in kitchens and bathrooms, treat water for drinking and keep swimming pools free of infectious agents.

Moreover, due to transport and handling safety concerns, the use of sodium hypochlorite is preferred over chlorine gas in water treatment, which represents a significant market expansion potential.[18]

Bleaching powder

Bleaching powder is any of various mixtures of calcium hypochlorite, lime (calcium hydroxide), and calcium chloride.[19] Also known as "chlorinated lime", it is used in many of the same applications as sodium hypochlorite, but is more stable and contains more available chlorine. It is usually a white powder. A purer, more stable form of calcium hypochlorite is called HTH or high test hypochlorite. Bleaching tablets contain calcium hypochlorite and other ingredients to prevent the tablets from crumbling. A supposedly more stable mixture of calcium hypochlorite and quicklime (calcium oxide) is known as "tropical bleach".[20] Percent active chlorine in these materials ranges from 20% for bleaching powder to 70% for HTH.

Chlorine

Chlorine is produced by the electrolysis of sodium chloride.

$$2\ NaCl + 2\ H_2O \rightarrow Cl_2 + H_2 + 2\ NaOH$$

Chlorine is used to prepare sodium and calcium hypochlorites. It is used as a disinfectant in water treatment, especially to make drinking water and in large public swimming pools. Chlorine was used extensively to bleach wood pulp, but this use has decreased significantly due to environmental concerns.

Chlorine dioxide

Chlorine dioxide, ClO_2, is an unstable gas and is used in situ or stored as dilute aqueous solutions. Despite these limitations it finds large-scale applications for the bleaching of wood pulp, fats and oils, cellulose, flour, textiles, beeswax, skin, and in a number of other industries. It can be prepared by oxidizing sodium chlorite with chlorine

$$2\ NaClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ NaCl$$

but more commonly it is prepared by reducing sodium chlorate with a suitable reducing agent like methanol, hydrogen peroxide, hydrochloric acid, or sulfur dioxide[21]

$$2\ NaClO_3 + 2\ HX + \text{"R"} \rightarrow 2\ NaX + 2\ ClO_2 + \text{"RO"} + H_2O$$

where "R" is the reducing agent and "RO" is the oxidized form.[22]

Peroxide-based bleaches

After chlorine-based bleaches, the peroxide bleaches are most commonly encountered. Peroxides are compounds that contain an oxygen-oxygen single bond, O-O. This is a fairly weak bond so reactions of peroxides often involve breaking this bond, giving very reactive oxygen species. Most peroxide bleaches are adducts of hydrogen peroxide. They contain hydrogen peroxide, HOOH in combination with another material like sodium carbonate or urea. An exception is sodium perborate, which has a cyclic structure containing two O-O single bonds. All peroxide-based bleaches release hydrogen peroxide when dissolved in water. Peroxide bleaches are often used with catalysts and activators, e.g., tetraacetylethylenediamine or sodium nonanoyloxybenzenesulfonate.

Hydrogen peroxide

Hydrogen peroxide is produced in very large amounts by several different processes. Its action as an oxidizer is why it is made and used in such large quantities. It is used by itself as a bleaching agent, for example to bleach wood pulp, hair and so on, or to prepare other bleaching agents like the perborates, percarbonates, peracids, etc.

Sodium percarbonate

Sodium percarbonate is produced industrially by reaction of sodium carbonate and hydrogen peroxide, followed by crystallization. Also, dry sodium carbonate may be treated directly with concentrated hydrogen peroxide solution.

$$2Na_2CO_3 + 3H_2O_2 \rightarrow 2Na_2CO_3.3H_2O_2$$

Dissolved in water, it yields a mixture of hydrogen peroxide (see above) and sodium carbonate. It is generally considered to be an eco-friendly cleaning agent.

Sodium perborate

Sodium perborate, $Na_2H_4B_2O_8$, is made by reacting borax with sodium hydroxide to give sodium metaborate ($NaBO_2$) which is then reacted with hydrogen peroxide to give hydrated sodium perborate.[23]

$$Na_2B_4O_7 + 2\ NaOH \rightarrow 4\ NaBO_2 + H_2O$$
$$2\ NaBO_2 + 2\ H_2O_2 + 6\ H_2O \rightarrow [NaBO_2(OH)_2 \text{ x } 3\ H_2O]_2$$

Sodium perborate is useful because it is a stable, source of peroxide anions. When dissolved in water it forms some hydrogen peroxide, but also perborate anion ($B(OOH)(OH)_3^-$), which is activated for nucleophilic oxidation.[24]

Miscellaneous bleaches

Peracetic acid and ozone are used in the manufacture of paper products, especially newsprint and white Kraft paper.[25] In the food industry, some organic peroxides (benzoyl peroxide, etc.) and other agents (e.g., bromates) are used as flour bleaching and maturing agents.

Reducing bleaches

Sodium dithionite (also known as **sodium hydrosulfite**) is one of the most important reductive bleaching agents. It is a white crystalline powder with a weak sulfurous odor. It can be obtained by reacting sodium bisulfite with zinc

$$2\ NaHSO_3 + Zn \rightarrow Na_2S_2O_4 + Zn(OH)_2$$

It is used as such in some industrial dyeing processes to eliminate excess dye, residual oxide, and unintended pigments and for bleaching wood pulp.

Reaction of sodium dithionite with formaldehyde produces Rongalite,

$$Na_2S_2O_4 + 2\ CH_2O + H_2O \rightarrow NaHOCH_2SO_3 + NaHOCH_2SO_2$$

which is used in bleaching wood pulp, cotton, wool, leather and clay.[26]

Environmental impact

A Risk Assessment Report (RAR) conducted by the European Union on sodium hypochlorite conducted under Regulation EEC 793/93 concluded that this substance is safe for the environment in all its current, normal uses.[27] This is due to its high reactivity and instability. Disappearance of hypochlorite is practically immediate in the natural aquatic environment, reaching in a short time concentration as low as 10^{-22} μg/L or less in all emission scenarios. In addition, it was found that while volatile chlorine species may be relevant in some indoor scenarios, they have negligible impact in open environmental conditions. Further, the role of hypochlorite pollution is assumed as negligible in soils.

Industrial bleaching agents can also be sources of concern. For example, the use of elemental chlorine in the bleaching of wood pulp produces organochlorines and persistent organic pollutants, including dioxins. According to an industry group, the use of chlorine dioxide in these processes has reduced the dioxin generation to under detectable levels.[28] However, respiratory risk from chlorine and highly toxic chlorinated byproducts still exists.

A recent European study indicated that sodium hypochlorite and organic chemicals (e.g., surfactants, fragrances) contained in several household cleaning products can react to generate chlorinated volatile organic compounds (VOCs).[29] These chlorinated compounds are emitted during cleaning applications, some of which are toxic and probable human carcinogens. The study showed that indoor air concentrations significantly increase (8–52 times for chloroform and 1–1170 times for carbon tetrachloride, respectively, above baseline quantities in the household) during the use of bleach containing products. The increase in chlorinated volatile organic compound concentrations was the lowest for plain bleach and the highest for the products in the form of "thick liquid and gel". The significant increases observed in indoor air concentrations of several chlorinated VOCs (especially carbon tetrachloride and chloroform) indicate that the bleach use may be a source that could be important in terms of inhalation exposure to these compounds. While the authors suggested that using these cleaning products may significantly increase the cancer risk,[30] this conclusion appears to be hypothetical:

- The highest level cited for concentration of carbon tetrachloride (seemingly of highest concern) is 459 micrograms per cubic meter, translating to 0.073 ppm (part per million), or 73 ppb (part per billion). The OSHA-allowable time-weighted average concentration over an eight-hour period is 10 ppm,[31] almost 140 times higher;
- The OSHA highest allowable peak concentration (5 minute exposure for five minutes in a 4-hour period) is 200 ppm,[31] twice as high as the reported highest peak level (from the headspace of a bottle of a sample of bleach plus detergent).

Disinfection

Sodium hypochlorite solution, 3–6%, (common household bleach) is typically diluted for safe use when disinfecting surfaces and when used to treat drinking water. When disinfecting most surfaces, 1 part liquid household bleach to 100 parts water is sufficient for sanitizing. Stronger or weaker solutions may be more appropriate to meet specific goals, such as destroying resistant viruses or sanitizing surfaces that will not be in contact with food. See references for more information.[32][33]

A weak solution of 2% household bleach in warm water is typical for sanitizing smooth surfaces prior to brewing of beer or wine.

US Government regulations (21 CFR Part 178) allow food processing equipment and food contact surfaces to be sanitized with solutions containing bleach, provided that the solution is allowed to drain adequately before contact with food, and that the solutions do not exceed 200 parts per million (ppm) available chlorine (for example, one tablespoon of typical household bleach containing 5.25% sodium hypochlorite, per gallon of water).

A 1-in-5 dilution of household bleach with water (1 part bleach to 4 parts water) is effective against many bacteria and some viruses, and is often the disinfectant of choice in cleaning surfaces in hospitals (primarily in the United States). The solution is corrosive, and needs to be thoroughly removed afterwards, so the bleach disinfection is sometimes followed by an ethanol disinfection. Even "scientific-grade", commercially produced disinfection solutions such as Virocidin-X usually have sodium hypochlorite as their sole **active** ingredient, though they also contain surfactants (to prevent beading) and fragrances (to conceal the bleach smell).[34]

See Hypochlorous acid for a discussion of the mechanism for disinfectant action.

Treatment of gingivitis [35]

Diluted sodium hypochlorite at a rate of 2000–1 (0.05% concentration) may represent an efficacious, safe and affordable antimicrobial agent in the prevention and treatment of periodontal disease.

Color safe bleach

Color safe bleach is a chemical that uses hydrogen peroxide as the active ingredient (to help remove stains) rather than sodium hypochlorite or chlorine.[36] It also has chemicals in it that help brighten colors.[37] Hydrogen peroxide is also used for sterilization purposes and water treatment, but its disinfectant capabilities may be limited due to the concentration in the colorsafe bleach solution as compared to other applications.[37]

See also

- Bleachfield
- Household chemicals
- Percent active chlorine
- Tooth whitening

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External links

- Bleach in (http://www.britannica.com/EBchecked/topic/69164/bleach) Britannica
- Bleach (MSDS) (http://www.florakim.com/files/Regular-Bleach-msds.pdf)

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