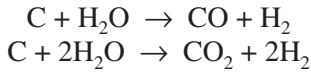


WATER GAS

Water gas is often called *blue gas* because of the color of the flame when it is burned. It is produced by the reaction of steam on incandescent coal or coke at temperatures above 1000°C.



The heating value of this gas is low (<300 Btu/ft³) and, to enhance it, oil may be atomized into the hot gas to produce *carbureted* water gas, which has a higher heat content.

WAX

Paraffin wax is a solid crystalline mixture of straight-chain (normal) hydrocarbons ranging from C_{20} to C_{30} and possibly higher, that is, $CH_3(CH_2)_nCH_3$ where $n \geq 18$. It is distinguished by its solid state at ordinary temperatures [$25^\circ C$ ($77^\circ F$)] and low viscosity [35 to 45 SUS at $99^\circ C$ ($210^\circ F$)] when melted. However, in contrast to petroleum wax, petrolatum (*petroleum jelly*), paraffin wax does in fact contain both solid and liquid hydrocarbons. It is essentially a low-melting, ductile, microcrystalline wax.

Paraffin wax from a solvent dewaxing operation is commonly known as *slack wax*, and the processes employed for the production of waxes are aimed at deoiling the slack wax (petroleum wax concentrate).

Wax sweating was originally used to separate wax fractions with various melting points from the wax obtained from shale oils and is still used to some extent, but is being replaced by the more convenient wax recrystallization process. In wax sweating, a cake of slack wax is slowly warmed to a temperature at which the oil in the wax and the lower melting waxes become fluid and drip (or sweat) from the bottom of the cake, leaving a residue of higher-melting wax.

Wax recrystallization, like wax sweating, separates slack wax into fractions, but instead of using the differences in melting points, it makes use of the different solubility of the wax fractions in a solvent, such as the ketone used in the dewaxing process. When a mixture of ketone and slack wax is heated, the slack wax usually dissolves completely, and if the solution is cooled slowly, a temperature is reached at which a crop of wax crystals is formed. These crystals will all be of the same melting point, and if they are removed by filtration, a wax fraction with a specific melting point is obtained. If the clear filtrate is further cooled, a second crop of wax crystals with a lower melting point is obtained. Thus, by alternate cooling and filtration, the slack wax can be subdivided into a large number of wax fractions, each with different melting points.

The melting point of paraffin wax has both direct and indirect significance in most wax utilization. All wax grades are commercially indicated in a range of melting temperatures rather than at a single value, and a range of 1°C (2°F) usually indicates a good degree of refinement. Other common physical properties that help to illustrate the degree of refinement of the wax are color, oil content, API gravity, flash point, and viscosity, although the last three properties are not usually given by the producer unless specifically requested.

Petroleum waxes (and petrolatum) find many uses in pharmaceuticals, cosmetics, paper manufacturing, candle making, electrical goods, rubber compounding, textiles, and many more.

WOOD CHEMICALS

Wood chemicals are derived from woody plants made of strong, relatively thick-walled long cells that make good fibers. The cell wall in this type of plant is a complex mixture of polymers that varies in composition. The solid portion of wood is over 95% organic material that is a mixture of three groups of polymers:

1. Cellulose, which is approximately 45% of the dry weight in an ordered array of high-molecular-weight glucose polymer chains, currently most valuable as fiber
2. Hemicellulose (20 to 25%), which is a disordered array of several sugar polymers for which there is currently no economical use except as fuel
3. Lignin (20 to 25%), which serves as binder for the cellulose fibers, and is a complex amorphous polyphenol polymer

Wood also contains extractives—organics removable with inert solvents—and the extracts vary with the species and the location in the tree.

Lignin has been described as *the adhesive material of wood* because it cements the fibers together for strength. It is a complex cross-linked polymer of condensed phenylpropane units joined together by various ether and carbon linkages. Lignin can be considered to be a polymer of coniferyl alcohol. About 50 percent of the linkages are β -aryl ethers. Lignin can be degraded with strong alkali, with an acid sulfite solution, and with various oxidizing agents. It is therefore removed from the wood to leave cellulose fibers, commonly called *pulp*. Although there are many differences between hardwood and softwood, the hardwoods always have less lignin and more hemicellulose (high in xylose), whereas the softwoods have more lignin and less hemicellulose (which is high in galactose, glucose, and mannose units). Besides the holocellulose and lignin of the cell wall, wood contains about 25% by weight of material that can be recovered by steam distillation or by solvent extraction.

In the kraft process (Fig. 1), the focus is a closed system with the exception of sodium sulfate being added periodically. Only wood enters the loop

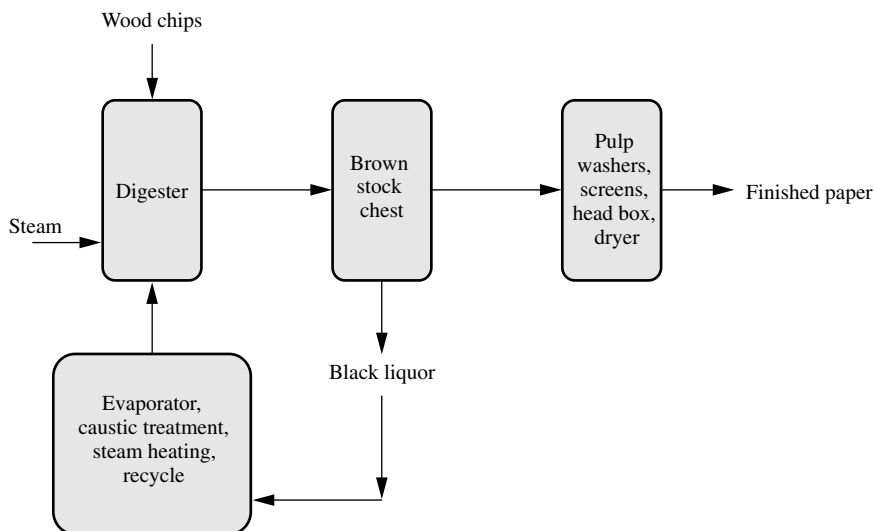


FIGURE 1 The kraft process.

and only pulp leaves. Digestion of the wood–white liquor mixture occurs at 170 to 175°C and 100 to 135 psi for 2 to 5 hours. A typical digester is 40 ft high with a diameter of 20 ft and can hold up to 35 tons of wood chips at a 1:4 wood: white liquor ratio.

The resulting pulp is separated from the black liquor (colored with organics), which is then oxidized to sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) and further oxidized in the furnace to sodium sulfate (Na_2SO_4). The organic material from the digestion process is oxidized in the furnace to carbon dioxide whereas the sodium sulfate is reduced back to sodium sulfide (Na_2S), the original oxidation state of sulfur in the process. The carbon dioxide is absorbed by sodium hydroxide (NaOH) to form sodium carbonate (Na_2CO_3). Water is added to the material from the furnace, forming a green liquor containing sodium hydrosulfide (NaSH) and sodium hydroxide. The sodium carbonate is reacted with calcium oxide (CaO) and water to give more sodium hydroxide (causticizing) and calcium carbonate (CaCO_3) which is usually filtered and transformed on site back into calcium oxide by a lime kiln.

After the crude pulp is obtained from the alkaline sulfate process, it is bleached in stages with elemental chlorine, extracted with sodium hydroxide, and oxidized with calcium hypochlorite, chlorine dioxide, and hydrogen peroxide. This lightens it from a brown to a light brown or even white (difficult) color. Chlorination of the aromatic rings of residual lignin is probably

what is occurring, although this has not been completely studied. Typical end uses of kraft pulp are brown bags, paper boxes, and milk cartons.

Much of the methyl mercaptan and dimethyl sulfide can be oxidized to dimethylsulfoxide, a useful side product that is a common polar, aprotic solvent in the chemical industry. This is in fact the primary method of its manufacture, as a kraft by-product. Caution must be used when handling it because of its extremely high rate of skin penetration.

Two other important side products of the kraft process are *turpentine* and *tall oil*. The turpentine is obtained from the gases formed in the digestion process. Tall oil soap is a black viscous liquid of rosin and fatty acids that can be separated from the black liquor by centrifuging. Acidification gives tall oil.

The *acid sulfite process* is used to obtain a higher-quality paper. It is also more water polluting. Digestion occurs in a mixture of sulfur dioxide and calcium or magnesium bisulfite. The magnesium bisulfite process is better for pollution but still not so good as the kraft process. Sulfite pulp is used for bond paper and high-grade book paper.

Wood is the source of a large number of chemicals and pharmaceuticals, and a number of lower-volume chemicals can be obtained from wood hydrolysis (Fig. 2). Furfural is formed from the hydrolysis of some polysaccharides to pentoses, followed by dehydration.

Furfural is used in small amounts in some phenol plastics; it is a small minor pesticide and an important commercial solvent. It can be converted into the common solvent tetrahydrofuran and an important solvent and intermediate in organic synthesis, furfuryl alcohol.

Vanillin is obtained from sulfite waste liquor by further alkaline hydrolysis of lignin. It is the same substance that can be obtained from vanilla bean extract and is the common flavoring in foods and drinks. Natural and synthetic vanillin can be distinguished from each other by a slight difference in the amount of ^{13}C in their structure, since one is biosynthetic in the bean and the other is isolated from a second natural product, wood, by hydrolysis of the lignin.

Charcoal was a valued commodity in antiquity. The ancient Egyptians used the volatile product of hardwood distillation, pyroligneous acid, for embalming. Before synthetic organic chemistry became well established, destructive hardwood distillation provided several important industrial chemicals, among these were acetone, acetic acid, and methanol (still often referred to as wood alcohol). Charcoal is a fine, smokeless fuel, prized for its smokeless nature and used extensively for outdoor cooking. Acetone was originally made by the dry distillation of calcium acetate made from wood-derived acetic acid, but better, cheaper sources are also available.

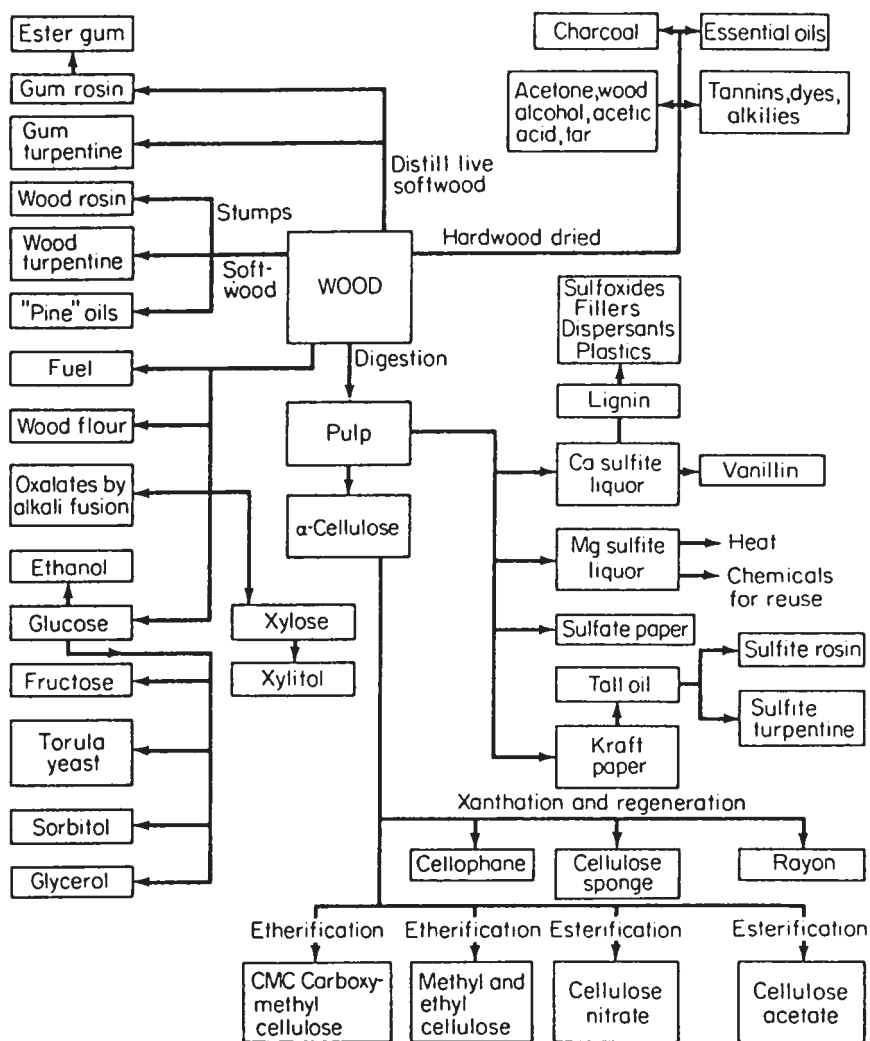


FIGURE 2 Chemicals from wood.

The manufacture of charcoal, especially briquettes, has been increasing. It is the residue after combustion of the volatiles from a hardwood distillation. It consists of elemental carbon and incompletely decomposed organic material and many adsorbed chemicals. Carbonization is usually performed at about 400 to 500°C. The charcoal has a volatile content of 15 to 25% by weight and can be made in about 37 to 46 percent yield by weight from wood.

See Pulp and Paper Chemicals, Tall Oil, Turpentine.

XENON

See Rare Gases.

XYLENES

The general term *xylenes* (*xylols*) refers to the C₈ aromatic isomers (CH₃C₆H₄CH₃) with the methyl groups in positions ortho, meta, and para to each other. Thus, the xylenes consist of three isomers: *o*-xylene, *m*-xylene, and *p*-xylene

The xylenes are colorless, flammable liquids with properties that are significantly different from each other or significantly similar to each other, depending upon the perspective and the need for separation of the isomers.

	Melting point	Boiling point	Density
<i>o</i> -xylene	-25°C	144.0°C	0.8968
<i>m</i> -xylene	-47.4°C	139.1°C	0.8684
<i>p</i> -xylene	13.2°C	138.5°C	0.8611

o-xylene (flash point: 27°C) can be separated from the *meta*-isomer (flash point: 27°C) and the *para*-isomer (flash point: 32°C) by distillation; the *para*-isomer and the *meta*-isomer are difficult to separate by distillation. The xylenes are insoluble in water, soluble in alcohol and ether.

The term *mixed xylenes* describes a mixture containing the three xylene isomers. Commercial sources of mixed xylenes include catalytic reformat, pyrolysis gasoline, toluene disproportionation product, and coke-oven light oil. Ethylbenzene is present in all of these sources except toluene disproportionation product.

In catalytic reforming, a low octane naphtha cut (typically a straight run or hydrocracked naphtha) is converted into high-octane aromatics, including benzene, toluene, and mixed xylenes. Aromatics are separated from the reformat by using a solvent such as diethylene glycol or sulfolane and then stripped from the solvent. Distillation is then used to separate the benzene-toluene-xylene into its components.

The amount of xylenes contained in the catalytic reformat depends on the fraction and type of crude oil, the reformer operating conditions, and the catalyst used. The amount of xylenes produced can vary widely, typically

ranging from 18 to 33% by volume of the reformat. In the United States, only about 12% of the xylenes produced via catalytic reforming are actually recovered for use as petrochemicals. The unrecovered reformat xylenes are used in the gasoline pool.

Pyrolysis gasoline is a by-product of the steam cracking of hydrocarbon feeds in ethylene crackers. Pyrolysis gasoline typically contains about 50 to 70% by weight of aromatics, of which roughly 50% is benzene, 30% is toluene, and 20% is mixed xylenes (which includes ethylbenzene).

Coke oven light oil is a by-product of the manufacture of coke for the steel industry. When coal is subjected to high-temperature carbonization, it yields 16 to 25 liters/ton of light oil that contains 3 to 6% by volume of mixed xylenes.

Xylenes can also be manufactured by the disproportionation of toluene (Fig. 1):



or by the transalkylation of toluene with trimethylbenzenes.



Toluene disproportionation is a catalytic process in which 2 moles of toluene are converted to 1 mole of xylene and 1 mole of benzene. Although the mixed xylenes from toluene disproportionation are generally more costly to produce than those from catalytic reformat or pyrolysis gasoline,

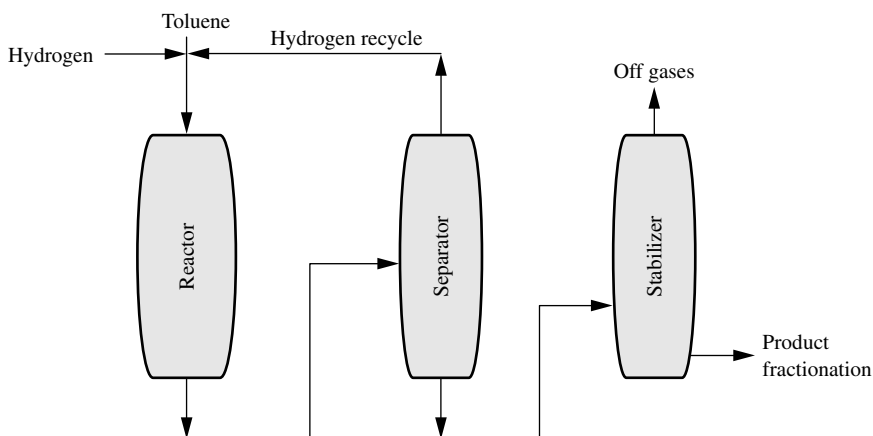


FIGURE 1 Xylene manufacture by the disproportionation of toluene.

their principal advantage is that they are very pure and contain essentially no ethylbenzene.

The manufacture of mixed xylenes and the subsequent production of high-purity *o*-xylene and *p*-xylene consists of a series of stages in which (1) the mixed xylenes are initially produced, (2) *o*-xylene and *p*-xylene are separated from the mixed xylenes stream, and (3) the *p*-xylene-depleted xylene stream is isomerized back to an equilibrium mixture of xylenes and then recycled back to the separation step.

The two principal methods for producing xylenes are catalytic reforming and toluene disproportionation.

In one process (Fig. 2), a light fraction (boiling range 65 to 175°C) from a straight run petroleum fraction or from an isocracker is fed to a catalytic reformer and is followed by fractionation and extraction. The mixed xylenes stream is then processed further to produce high-purity *p*-xylene and/or *o*-xylene. Because of the close boiling points of *p*-xylene and *m*-xylene, production of high-purity *p*-xylene by distillation is impractical and methods such as crystallization and adsorption are used.

In the separation of the xylenes, the C₈ mixture is cooled to -70°C in the heat exchanger refrigerated by ethylene. Because of the difference in melt-

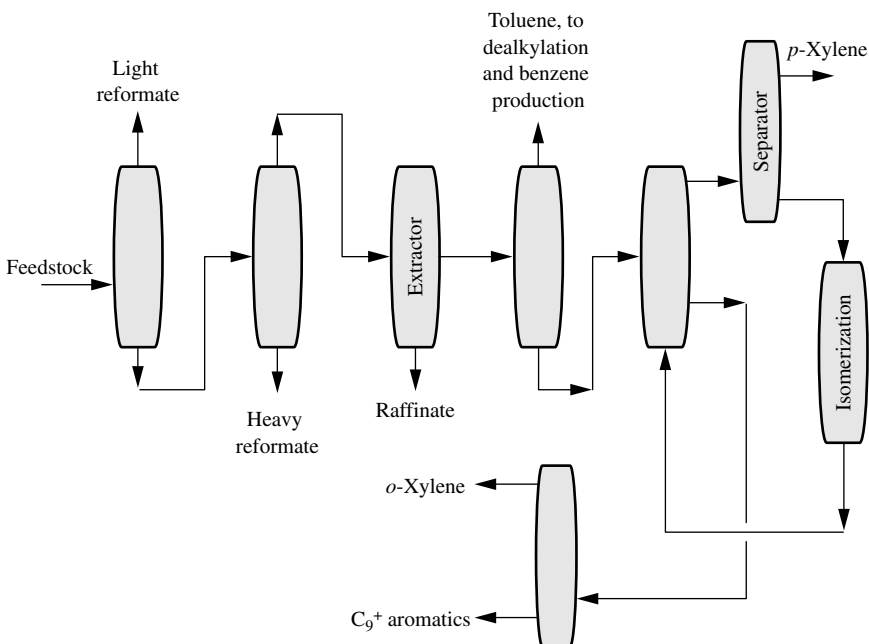


FIGURE 2 Manufacture of xylenes by catalytic reforming and toluene disproportionation.

ing points (*o*-xylene -25.0°C ; *m*-xylene -47.9°C ; *p*-xylene 13.2°C), the para-isomer crystallizes preferentially. The other two isomers remain liquid as a mixture and the solid para-isomer is centrifuged and separated. A second cooling cycle needs only propane as coolant, and complete separation is accomplished with an optional third cooling cycle.

Because of the large demand for *p*-xylene, another method is now being used to increase the percentage of the para-isomer in mixed xylenes. They are heated at 300°C with an acidic zeolite catalyst, which equilibrates the three xylenes to an *o*, *m*, *p* ratio of 10:72:18. The para-isomer is separated by fractional crystallization, whereas the ortho-meta mixture is reisomerized with the catalyst to produce more para-isomer.

Another possibility for separating the para-isomer involves selective adsorption on zeolites, then desorption after the ortho and meta isomers have been separated. The slightly different boiling point of the *o*-xylene is the basis for separation from the other two isomers through an elaborate column.

After separation of the preferred xylenes, i.e., *p*-xylene or *o*-xylene, the remaining raffinate stream, which tends to be rich in *m*-xylene, is typically fed to a xylenes isomerization unit in order to further produce the preferred xylenes. Isomerization units are fixed-bed catalytic processes that are used to produce a close-to-equilibrium mixture of the xylenes. To prevent the buildup of ethylbenzene in the recycle loop, the catalysts are also designed to convert ethylbenzene to either benzene and xylenes or to benzene and diethylbenzene.

Historically, the isomerization catalysts have included amorphous silica-alumina, zeolites, and metal-loaded oxides. All of the catalysts contain acidity, which isomerizes the xylenes and if strong enough can also crack the ethylbenzene and xylenes to benzene and toluene.

The xylenes can be used as a mixture or separated into pure isomers, depending on the application. The mixture is obtained from catalytic reforming of naphtha (using a platinum catalyst) and separated from benzene and toluene by distillation.

p-xylene is used in the manufacture of terephthalic acid, which is reacted with ethylene glycol to give poly (ethylene terephthalate). Large amounts of this polyester are used in textile fibers, photographic film, and soft drink bottles.

o-xylene is used in the manufacture of phthalic anhydride, an intermediate in the synthesis of plasticizers, substances that make plastics more flexible. A common plasticizer is dioctyl phthalate.

See Benzene and Ethylbenzene.

ZINC CHROMATE

Zinc chromate (ZnCrO_4), also known as zinc yellow (with the approximate formula $4\text{ZnO} \cdot \text{K}_2\text{O} \cdot 4\text{CrO}_3 \cdot 3\text{H}_2\text{O}$), is used as a pigment because of its excellent corrosion-inhibiting effect both in mixed paints and as a priming coat for steel and aluminum.

ZINC OXIDE

Zinc oxide (ZnO) is manufactured by oxidizing zinc vapor in burners in which the concentration of zinc vapor and the flow of air are controlled to produce the desired particle size and shape. The hot gases and particulate oxide or fume pass through tubular coolers, and then the zinc oxide is separated in a baghouse. The purity of the zinc oxide depends upon the source of the zinc vapor.

In the *indirect process*, zinc metal vapor for burning is produced in several ways, one of which involves horizontal retorts. Since the entire vapor is burned in a combustion chamber, the purity of the oxide depends on that of the zinc feed. Oxide of the highest purity requires special high-grade zinc, and less-pure products are made by blending in Prime Western and even scrap zinc.

In the *direct process*, four or more firebrick furnaces having common walls are charged in cyclic fashion. Coal that is hot from the previous charge is first spread on the grate and, after ignition, a damp, well-blended mixture of zinc ore or zinc-containing material and coal is added. The bed is maintained in a reducing condition with carbon monoxide to produce zinc and lead, if present. Metal vapors are drawn into a chamber above the furnace, where combustion air oxidizes them to pigment. The hot pigment-gas stream enters a cooling duct common to the whole block and, in this way, the product becomes a uniform blend.

Traveling-grate furnaces can also be employed. In this process, anthracite briquettes are fed to a depth of about 15 cm. After ignition by the previous charge, the coal briquettes are covered by ore/coal briquettes. The latter are dried with waste heat from the furnace. Zinc vapor evolves and burns in a combustion chamber, and the spent clinker falls into containers for removal.

A pigment-grade zinc oxide rotary kiln uses high temperature to produce pigment-quality zinc oxide and makes possible higher recovery than a grate furnace.

Other processes include an *electrothermic process*, an electric-arc vaporizer process, and the slag fuming process.

Zinc oxide, as an amphoteric material, reacts with acids to form zinc salts and with strong alkali to form zincates. In the vulcanization of rubber, the chemical role of zinc oxide is complex and the free oxide is required, probably as an activator.

Zinc oxide reacts with organic acids to produce zinc soaps and also reacts with carbon dioxide in moist air to form oxycarbonate. Acidic gases, e.g., hydrogen sulfide, sulfur dioxide, and chlorine, react with zinc oxide, and carbon monoxide or hydrogen reduce it to the metal. At high temperatures, zinc oxide replaces sodium oxide in silicate glasses. An important biochemical property of the oxide is its fungicidal/mildewstatic action. It is also soluble in body fluids and soils.

Zinc oxide of high purity is required for pharmaceutical, photoconductive, and certain other uses, and is manufactured by the indirect process. Less-pure zinc oxide is manufactured by the direct process, by which impure zinc oxide is reduced to zinc vapor that is then burned.

ZINC SULFATE

See Lithopone.

ZINC SULFIDE

See Lithopone.